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# Particulate Matter Air Monitoring Network in the San Francisco Bay Area: Assessment and Management Recommendations

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# Particulate Matter Air Monitoring Network in the San Francisco Bay Area: Assessment and Management Recommendations

**María del Carmen Durán**

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for the degree of:

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**Received**

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## ABSTRACT

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Particulate matter is one of six criteria pollutants regulated by the U.S. EPA. The purpose of this paper is to evaluate the current particulate matter ( $PM_{10}$  and  $PM_{2.5}$ ) air monitoring network operated by the Bay Area Air Quality Management District (BAAQMD), or Air District, and to make management recommendations on how the air monitoring network may be improved. Improving the air monitoring network can lead to a better understanding of sources of particulates in the San Francisco Bay Area, which could lead to better modeling and more effective mitigation of pollutants. This paper focuses on seven sites across nine counties in the San Francisco Bay Area. Data from the seven sites were gathered from the Air District and a U.S. EPA database, which included mass concentration, ion speciation, organic and elemental carbon composition, and metals speciation for both  $PM_{10}$  and  $PM_{2.5}$ . Monthly averages ranging from 2011-2015 of these components were analyzed and used to evaluate whether the Air District was effectively monitoring for particulates. Results show that the San Francisco Bay Area should focus on  $PM_{2.5}$  analysis, as  $PM_{10}$  levels are significantly lower than the National Ambient Air Quality Standard. While  $PM_{2.5}$  is the primary particulate matter class of concern,  $PM_{10}$  still needs to be monitored because of monitoring requirements, but utilizing beta attenuation monitors (BAMs) technology will be an acceptable substitute.

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## DEFINITIONS (ACRONYMS)

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AQS	Air Quality System
BAAQMD	Bay Area Air Quality Management District
BAM	Beta Attenuation Monitor
BC	Black Carbon
CAA	Clean Air Act
CAAQS	California Ambient Air Quality Standards
CBSA	Core-based Statistical Areas
CFR	Code of Federal Regulations
CSN	Chemical Speciation Network
EC	Elemental Carbon
EPA	Environmental Protection Agency
FEM	Federal Equivalent Method
FRM	Federal Reference Method
IC	Ion Chromatography
µm	Micrometers or microns
µg/m <sup>3</sup>	Micrograms per cubic meter, measure of concentration
MSA	Metropolitan Statistical Areas
NAAQS	National Ambient Air Monitoring Standards
NAMS	National Air Monitoring Station
NATTS	National Air Toxics Trends Station
NCore	National Core Monitoring Program
NO <sub>3</sub> <sup>-</sup>	Nitrate Ion
OC	Organic Carbon
OC/EC	Organic Carbon/Elemental Carbon Analyzer
OMB	U.S. Office of Management and Budget
PM <sub>10-2.5</sub>	Particulate matter 2.5 µm to 10 µm in aerodynamic diameter
PM <sub>10</sub>	Particulate matter 10 µm in aerodynamic diameter and smaller
PM <sub>2.5</sub>	Particulate matter 2.5 µm in aerodynamic diameter and smaller
PM <sub>2.5C</sub>	Continuous PM <sub>2.5</sub> monitoring using a BAM
PM <sub>2.5F</sub>	Filter-based PM <sub>2.5</sub> monitoring
PQAO	Primary Quality Assurance Organization
SASS	Speciation Air Sampling System
SIP	State Implementation Plan
SLAMS	State and Local Air Monitoring Station
SO <sub>4</sub> <sup>2-</sup>	Sulfate Ion
SPM	Special Purpose Monitoring
STN	Speciation Trends Network
TSP	Total Suspended Particulates



XRF | X-Ray Fluorescence

## 1. INTRODUCTION

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Air quality is important and relevant in the context of environmental management because air quality significantly impacts both the quality of the human life and the environment. Poor air quality diminishes one's health and results in the deterioration of nature. Ineffective monitoring for particulate matter prevents regulatory agencies, such as the Air District, from understanding the constituents of poor air quality. The current air monitoring network has lacked a thorough network evaluation, as speciation data had not been studied for the last network assessment in 2015, only mass concentration data was studied for both  $PM_{10}$  and  $PM_{2.5}$  (Bay Area Air Quality Management District, 2015). Similarly, sized air districts like South Coast Air Quality Management District have shifted away from filter-based  $PM_{10}$  monitoring to continuous monitoring stations. Although the air monitoring network is evaluated according to specific Environmental Protection Agency (EPA) criteria every five years, the ozone air monitoring network has been given a more thorough evaluation than particulate matter network. More resources at the Air District are spent speciating  $PM_{10}$  filters than  $PM_{2.5}$  even though  $PM_{2.5}$  is more of a health concern.

The general topic for this research paper is particulate matter and the San Francisco Bay Area's current air monitoring network for  $PM_{10}$  and  $PM_{2.5}$ , and whether the Bay Area Air Quality Management District (BAAQMD), or Air District, is adequately and effectively monitoring particulate matter. This analysis will determine if there needs to be as thorough of a focus on performing chemical speciation on  $PM_{10}$  filters, when  $PM_{2.5}$  is more of a health concern, and more of a problem in the San Francisco Bay Area than  $PM_{10}$  pollution. This research paper will look at the chemical speciation data and look at how the air monitoring network could be improved with management recommendations.

This technical data analysis will use data from the Air District and compare what has been collected for both  $PM_{10}$  and  $PM_{2.5}$ . The examined data collections will include mass concentration; ion concentration for ammonium, potassium, chloride, nitrate, and sulfate; carbon concentration and ratios for elemental (black) carbon and organic carbon; and metals concentrations of lead, cadmium, and nickel. The chemical speciation and mass concentration data between  $PM_{10}$  and  $PM_{2.5}$  will be assessed to evaluate if there is enough significance between the two different classifications to justify continuing filter-based  $PM_{10}$  analysis. To get the best representation of data, it is important to look at five years' worth of data. Data from January 1,

2011 to December 31, 2015 will be used in this analysis. A five-year period allows for considering severe drought years or years with an abnormally high precipitation, which could skew the data.

The data will be extracted from the Air District's Data Management System and servers, as well as EPA's Air Quality System. The data will consist of 24-hour average data, either from daily measurements from continuous monitors or from filters that have been sampled on a schedule of every six days or every 12 days, as determined by EPA. The 24-hour average data will then be averaged into monthly averages to manage to daily averages easier. This paper will look to answer if the Air District is effectively monitoring for particulate matter, and if the Air District is not monitoring effectively, how could the particulate matter air monitoring network be better improved by looking at the mass concentration and chemical speciation data from 2011 to 2015. This paper will help determine if continuing to chemically speciate PM<sub>10</sub> is an effective use of resources, and if using continuous monitors would be more logical as continuous monitors will allow the Air District to collect more PM<sub>10</sub> data. The increased amount of daily concentrations of PM<sub>10</sub> would allow for a better understanding of how incidences impact the concentration of coarse particulates in the San Francisco Bay Area since collecting samples every six or 12 days could miss days where there are incidences such as refinery flaring or wildfires.

## 2. BACKGROUND

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### 2.1. DEFINITION OF PM<sub>2.5</sub> AND PM<sub>10</sub>

Particulate matter consists of liquid droplets or solids that vary in size, chemical, and physical composition (U.S. EPA, 2015). There are two types of particulate matter that are monitored by air districts across the nation, as required by the Environmental Protection Agency (EPA): PM<sub>10</sub> and PM<sub>2.5</sub>. PM<sub>10</sub> are particulates that have an aerodynamic diameter of 10 µm and smaller, whereas PM<sub>2.5</sub> particulates have an aerodynamic diameter of 2.5 µm and smaller (U.S. EPA, 2017a). Particulates 2.5 µm and smaller are often referred to as fine particulates. Particulates that range from 2.5 µm to 10 µm are often referred to as coarse particulates, designated as PM<sub>10-2.5</sub>. Both PM<sub>10</sub> and PM<sub>2.5</sub> are considered criteria air pollutants, or criteria pollutants. Particulate matter is one of criteria pollutants listed under the Clean Air Act, which defines common and harmful air pollutants (U.S. EPA, 2015). There are two additional types of particulates that can be monitored by air districts: total suspended particulates (TSP) and ultra-fine particulates. However, the scope of this paper will only discuss PM<sub>10</sub>, PM<sub>10-2.5</sub>, and PM<sub>2.5</sub>.

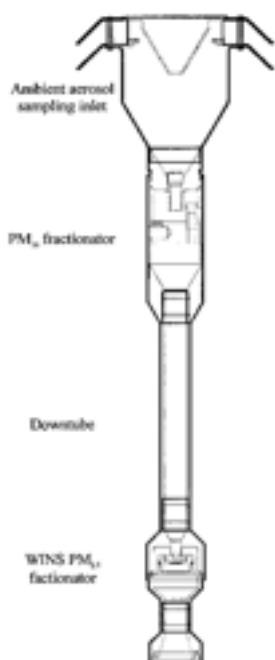
Airborne particulates result from direct emissions from a point source that form due to chemical reactions and phase changes in the atmosphere (Seinfeld & Pandis, 2016). Particulates in the troposphere are typically comprised of ions (sulfate, ammonium, nitrate, sodium, chloride), trace metals, organic carbon, elemental carbon, and water (Seinfeld & Pandis, 2016). The majority of particulates in the troposphere, the section we inhabit, are the result of human activities (Seinfeld & Pandis, 2016). PM<sub>10</sub> originates from farms, mines, roads, and pollen (Hill, 2009). Additionally, coarse particulates can result from mechanical processes, such as grinding of concrete (Seinfeld & Pandis, 2016). PM<sub>2.5</sub> is the result of incomplete combustion from sources such as diesel vehicles, electric power plants, and industrial processes such as petroleum refineries (Hill, 2009). Wood and biomass burning, construction, and sea salts can also contribute to both particulate levels (Hill, 2009). Further discussion of the chemical makeup of particulates and how the composition varies with particulate size will be discussed in the results of this paper.

### 2.2. PARTICULATE MATTER MONITORING

In order to accurately monitor particulate levels, the EPA has designated two different types of methods for analyzing monitoring for both PM<sub>10</sub> and PM<sub>2.5</sub>: the Federal Reference

Method (FRM) and the Federal Equivalent Method (FEM). For both  $PM_{10}$  and  $PM_{2.5}$ , the FRM is a filter-based method that monitors for a 24-hour period from midnight to midnight on a schedule as determined by the EPA (Noble et al., 2001; U.S. EPA, 2017b). FEM involves a continuous air monitor, a beta attenuation monitor (BAM) which is able to monitor and produce real-time data every minute (Noble et al., 2001; U.S. EPA, 2017b). BAMs were approved for use by the EPA as an equivalent method in 2008 (Tao & Harley, 2014). More details on how mass concentrations are calculated for both FRM and FEM methods can be found in Section 4.1, Methodology, as well as more information on how the instrumentation functions. Instruments used for regulatory purposes need to abide by performance-based criteria to ensure accurate data, which can be found in Part 53 of Title 40 of the Code of Federal Regulations (CFR).

Filter based analysis of particulates for mass concentration is typically the federal reference method, whereas continuous based monitors, specifically BAMs, are the approved federal equivalent method. The Air District utilized both technologies to analyze particulates in the San Francisco Bay Area. All high volume  $PM_{10}$  analysis is done using the filter based approach.  $PM_{2.5}$  analysis is performed using both continuous monitoring technology and filter based monitors. There are other technologies that exist to monitor for particulates; however, for the purpose of this project, only sampling methods related to the data that is being analyzed will be discussed.



**Figure 1.** Diagram of a  $PM_{2.5}$  FRM sampler head that pulls particulates onto a filter (Noble et al., 2001).

Figure 1 shows the sampler head for a PM<sub>2.5</sub> FRM sampler. The air flows in through the sampling inlet at a regulated rate, then passes through the PM<sub>10</sub> fractionator, which removes particulates greater than 10 µm in aerodynamic diameter. The air continues through the down-tube and then through the PM<sub>2.5</sub> fractionator, which removes particulates greater than 2.5 µm in aerodynamic diameter. This PM<sub>2.5</sub> fractionator ensures that only particulates 2.5 µm in diameter and below are sampled onto a filter. For the purposes of FRM PM<sub>2.5</sub>, the particulates are sampled onto a teflon filter (U.S. EPA, 2017a). The PM<sub>10</sub> FRM sampler head works in a similar fashion, without the PM<sub>2.5</sub> fractionator. High volume (approximately 1600-1700 m<sup>3</sup>) PM<sub>10</sub> can be sampled on to quartz fiber filters if they are, whereas low volume (24 m<sup>3</sup>) samples are commonly sampled on teflon filters (U.S. EPA, 2017a). These filters are conditioned and weighed in a temperature and humidity controlled room prior to sampling and then conditioned again and weighed after sampling has occurred in the same temperature and humidity controlled room (U.S. EPA, 2017a). The formula for mass concentration can be seen below.

**Formula 1.**  $\text{mass concentration } \left( \frac{\mu\text{g}}{\text{m}^3} \right) = \frac{\text{mass of particles on filter } (\mu\text{g})}{\text{volume of air passed through filter } (\text{m}^3)}$

BAMs have similar sampling heads and work similarly. Instead of sampling onto a filter that needs to be weighed, particulates are sampled onto filter tape (Schweizer et al., 2016). The particulates are then measured by taking a measurement of a sampled on area and a clean surface of the filter tape using beta attenuation to calculate the concentration of particulates (Schweizer et al., 2016). Beta attenuation is the method in which beta radiation is emitted and is absorbed and the readings are converted into mass concentration (Tao & Harley, 2014; Triantafyllou et al., 2016). Both PM<sub>10</sub> and PM<sub>2.5</sub> can be monitored using beta attenuation, with a specific fractionator to separate the particulates that are above the desired particulate size cut.

### 2.3. COMPARISON OF ANALYTICAL TECHNIQUES

Studies have been performed to evaluate the comparability of the FRM and FEM techniques of mass concentration analysis for PM<sub>10</sub> and PM<sub>2.5</sub>. One study compared analytical techniques for measuring the concentration of particulates in southeastern Italy, looking at gravimetric (FRM), beta attenuation (FEM), and two other non-FEM techniques were compared to evaluate if the techniques are statistically the same (Dinoi et al., 2015). The authors found that the correlation coefficient, or R<sup>2</sup>, between the FRM and FEM techniques for PM<sub>10</sub> was 0.98 and

for  $PM_{2.5}$  was 0.99 (Dinoi et al., 2015). These correlation coefficients show that both methods of analysis (FRM and FEM) can be compared because they are statistically similar.

In a similar study performed in Athens, Greece, the authors studied and compared particulate matter mass concentrations measurements between gravimetric and beta attenuation methods and discussed factors that could influence measurements of both  $PM_{10}$  and  $PM_{2.5}$  (Triantafyllou et al., 2016). In the Athens study, the authors found that the correlation coefficients for the comparison of gravimetric analysis and BAMs was 0.82 on a teflon filter (Triantafyllou et al., 2016). The authors also discussed how correlation varies slightly dependent on the type of filter used for gravimetric analysis (teflon, quartz and glass fiber), as they absorb water differently and because the BAMs they used in the study used glass fiber filter tape (Triantafyllou et al., 2016). Teflon filters are less affected by moisture in the air than quartz and glass fiber filters, and moisture content affects the accuracy of mass measurement (Triantafyllou et al., 2016). The authors found a correlation coefficient of 0.90 for the comparison of  $PM_{10}$  gravimetric analysis on teflon filters to BAMs (Triantafyllou et al., 2016). The reported correlation coefficients show that there is a good correlation between the gravimetric analysis and BAMs analysis, thus indicating that the two methods are comparable.

In a study performed in California, data was pulled from six different sites across California from 2009 to 2011: West Oakland, San José, Fresno, Bakersfield, Long Beach, and Riverside (Tao & Harley, 2014). The study looked at the correlation between BAMs and filter-based  $PM_{2.5}$  monitors to evaluate if the FRM and FEM types of monitors could be compared (Tao & Harley, 2014). Both the San José and West Oakland sites are in the Air District's jurisdiction, and are also sites that were studied in the previous section, though the timeframe of the study was different. For all six sites the correlation coefficients ranged from 0.83 to 0.96 (Tao & Harley, 2014). All the correlation coefficient values show that there is a good correlation between the BAMs and filter  $PM_{2.5}$  concentration data (Tao & Harley, 2014). The authors did find that the  $PM_{2.5}$  concentrations had a tendency to be higher for the BAMs than for the filter measurements, though because there were only filter values once every three or six days it is uncertain if the higher values for BAMs is true every day (Tao & Harley, 2014).

One possible reason for the discrepancy in BAM and filter-based  $PM_{2.5}$  concentrations is that particulate matter is partially composed of ammonium nitrate particulates, which are volatile (Tao & Harley, 2014). The volatility would be seen greater on filter-based samples because the

filters must be transported to a laboratory to weigh the filters, whereas with BAMs, measurements are taken instantaneously, which does not allow for as much of the ammonium nitrate to volatilize. California and the western coast of the United States have a higher percentage of ammonium and nitrate in  $PM_{2.5}$ , which would contribute to loss of mass due to volatilization and the slight discrepancy in concentrations between BAMs and filters (Tao & Harley, 2014). In addition to the ammonium nitrate volatility, there is also an issue with particulates that have a higher organic carbon content (Vega et al., 2003). Higher organic carbon content could be an indicator of a higher semi-volatile and/or volatile organic compounds being present, which could volatilize in the transport of filters to the laboratory for analysis (Vega et al., 2003). The discrepancy between BAMs and filter-based  $PM_{2.5}$  concentrations could also be applied to  $PM_{10}$  filter-based monitoring. The same principle of volatility would apply to  $PM_{10}$  filters if the  $PM_{10}$  particulates on the filters have ammonium, nitrate, or semi-volatile/volatile organic compounds. While the EPA requires filters to be transported below 4°C after the filters have been sampled on, it is still possible that ammonium, nitrate, or semi-volatile/volatile organic compounds would still volatilize off the filters.

One concern that can arise with filter-based monitoring is that filters are sampled on a designated scheduled determined by the EPA, and filters sample either every three days, every six days or every 12 days (U.S. EPA, 2017c). Specifically for  $PM_{10}$  analysis, the filters that are for SPM sites are run every 12 days and the SLAMS sites are run every six days (Knoderer, Nguyen, Alrick, & Hoag, 2016). SASS  $PM_{2.5}$  sites are run every six days whereas the  $PM_{2.5}$  site in San José samples every three days (Knoderer et al., 2016). Continuous monitors are designed to run every day and provide data instantaneously. Only collecting data a few times a month can skew data and miss days where there are unusually high or low levels of particulates, or reversely, can skew the data and have sampling days on days of abnormally high particulates. For example, there were some months of  $PM_{10}$  data that there was only one valid day of data. Additionally, having so few scheduled sampling days in a month means that if an incident causes a filter to be invalidated, such as a power outage or damaged filter, there will be less valid data to use for network assessment. A BAM can also have issues with invalidated data. Power outages and filter tape jams are issues that can cause loss of data (Tao & Harley, 2014). However, the percentage of data will usually be higher with BAMs even if an event causes invalidated data. Sampling every day could also be useful in instances of where there is an event that results in a



risk of harm to the general public, such as a refinery fire or the various wildfires that have affected the San Francisco Bay Area and the rest of California. In recent years, the current practice is to have field staff rush to set up filters for sampling, which may not be collecting the worst of the exposure to particulates. Additionally, utilizing continuous monitors allows for a more complete set of data and could lead to a better understanding of particulate matter concentrations and sources of particulates.

There were two analytical techniques used in monitoring for organic and elemental (black) carbon: aethalometer and an OC/EC. As mentioned previously, aethalometers are the continuous monitors that are currently used to monitor for black/elemental carbon, while the OC/EC is the laboratory instrument used to analyze organic and elemental carbon from sampled on filters. One issue with analyzing organic and elemental carbon using the OC/EC is that depending on the heating method and correction for pyrolysis (crystalline carbon formed in the analysis), values can vary significantly (Quincey et al., 2009). In addition, the filters themselves and samples could have mineral oxides that also impact the values (Quincey et al., 2009). One study the authors performed in Scotland showed that there was a correlation coefficient of 0.79 for elemental carbon measurements between the OC/EC and the aethalometer (Quincey et al., 2009). However, the authors hypothesized that the OC/EC was over-correcting for the pyrolysis and that the OC/EC would actually underestimate the actual amount of elemental carbon, which would be insignificant for near-road monitors, but significant for rural sites (Quincey et al., 2009). One limitation for the use of an aethalometer is that it can only identify fossil fuels and biomass burnings when measuring for elemental carbon (Briggs & Long, 2016).

One final area of concern when using filters for particulate matter analysis, specifically when using the PM<sub>10</sub> quartz fiber filters, is the difference of using a high volume versus low volume sampling method and the issue of the size and fragility of the PM<sub>10</sub> quartz fiber filters. One study found that there was higher uncertainty in measurements when high volume samples were taken using a high flow rate, and the authors recommend when using a high volume sampler, to run the sample at a lower flow rate (Lacey & Faulkner, 2015). The Air District currently uses a high volume, high flow rate for all the PM<sub>10</sub> sites that use quartz fiber filters. Additionally, the study found that there is uncertainty in measuring drops in pressure across the flow meter during calibration and during sample collection (Lacey & Faulkner, 2015). The uncertainty in flow rate and the fluctuations that occur can result in an inaccurate air volume,

which is used to calculate concentrations, and can also result in the uneven sampling across the quartz fiber filter, which can impact the analysis for ionic and organic/elemental carbon content as the whole filter is not used for those analyses, just a small portion of the filters. Due to these uncertainties, there is an inherent uncertainty in the reported results for the PM<sub>10</sub> speciation components. The results could be artificially high or low, and it is difficult to ascertain how much of an impact the uncertainty in the air volumes and uneven sampling have on the results. Low volume particulate matter sampling does not experience the same uncertainties, which can mean low volume particulate matter sampling is more reliable than high volume sampling. Additionally, as someone who has worked with the types of filters being discussed in this paper, the high volume PM<sub>10</sub> quartz fiber filters are fragile. This issue is not well documented in journal articles. However, in discussing this issue with other more senior laboratory, air monitoring, and quality assurance personnel, the fragility is well known among those in the air monitoring field. The filters have a habit of shedding quartz fibers and the corners where the filter occasionally time to time.

According to the literature reviewed, beta attenuation monitors have proven to be reliable and comparable instruments for the monitoring of particulate matter mass concentration for both PM<sub>10</sub> and PM<sub>2.5</sub>. South Coast Air Quality Management District, whose jurisdiction is most comparable with the Bay Area Air Quality Management District in California, currently uses BAMs to monitor for both PM<sub>10</sub> and PM<sub>2.5</sub> mass concentration, where the Air District only uses BAMs for monitoring PM<sub>2.5</sub> mass concentration. The literature reviewed indicates that the values for filter based PM<sub>10</sub> and BAMs PM<sub>10</sub> are statistically similar and, if the results of the analysis in this paper shows that chemical speciation of PM<sub>10</sub> is redundant, the Air District should have no issue with data reproducibility if the agency decided to switch to the BAMs. The BAMs allow for continuous monitoring of PM<sub>10</sub>, which is not currently available with the filter based monitoring method. The analysis in this paper will help determine if the Air District needs to continue to speciate PM<sub>10</sub> filters, and if not, BAMs can become a suitable replacement.

## 2.4. OVERVIEW OF THE PARTICULATE MATTER AIR MONITORING NETWORK

There are rules and regulations that need to be abided by in planning where air monitoring sites are placed and what should be monitored at these sites such as particulates and/or ozone. The Air District, not only abides by federal, state and local regulations, but also abides by its own objectives. Some examples of regulations include meeting federal and state

standard levels for particulates and meeting the minimum number of monitoring sites in a designated location.

Locally, the Air District works to better the air quality in the San Francisco Bay Area. The Air District's agency wide mission statement is "to create a healthy breathing environment for every Bay Area resident while protecting and improving public health, air quality, and the global climate" (Bay Area Air Quality Management District, 2016). To achieve its mission statement, the Air District has strategic goals including the reduction of health issues resulting from poor air quality, and ensuring that the Air District meets state and national regulatory standards for criteria pollutants (Bay Area Air Quality Management District, 2016). The Air District also strives to produce quality regulatory programs that help meet federal, state, and local regulations and to take a lead role in rule development and making information about pollution levels and sources publicly available (Bay Area Air Quality Management District, 2016). The Air District offers incentives such as vehicle buyback programs, engages and partners with the community to reduce mobile emissions, and improve land-use planning and energy efficiency and to help reduce their own emissions such as wood burning and driving, on a daily basis through community engagement meetings and workshops (Bay Area Air Quality Management District, 2016). The Air District intends to use advanced technology, such as real-time pollutant data streaming to the Air District's website, in their daily operations to maintain an efficient and effective agency (Bay Area Air Quality Management District, 2016).

Additionally, the Air District has specific air monitoring objectives they adhere to (Knoderer et al., 2016). The first air monitoring objective is to make air monitoring data publicly available in a timely manner. The second air monitoring objective is to maintain compliance with the California and National Ambient Air Quality Standards (NAAQS) and develop attainment plans when sites within their jurisdiction do not meet these standards. The third and final air monitoring objective is to participate in air quality research. Both the agency wide objectives as well as the specific air monitoring objectives give the framework on the Air District's process of choosing their air monitoring sites. It is important to keep these objectives in mind when discussing how the particulate matter air monitoring network can be improved.

There are multiple factors to be taken into consideration when designing an air monitoring network, particularly the regulatory requirements that an air district must adhere to monitor pollutants. These regulatory requirements include meeting the ambient air quality

standards, meeting the minimum monitoring requirements that are determined by population size, and meeting the requirements for EPA trends programs. The EPA started regulating particulates in 1971 by monitoring total suspended particulates (TSP) with the National Ambient Air Quality Standards or NAAQS (U.S. EPA, 2016). There are primary and secondary standards listed for most criteria pollutants under the Clean Air Act. Primary standards are determined and set to protect the public health, whereas secondary standards are set to protect public welfare, which includes visibility, as well as protecting animals, agriculture, vegetation and infrastructure (U.S. EPA, 2017a).

Particulate matter standards are presented in two different methods: 24-hour daily averages and annual averages. The 24-hour daily average is the concentration of particulates collected from 00:00 to 24:00 (midnight to midnight) on a sampling day. Standards need to be met to remain in attainment. Attainment is when a geographic area meets the NAAQS for a given criteria pollutant, whereas non-attainment is when geographic areas exceed the NAAQS. In 1971, the EPA set the first particulate matter primary standards for TSP at  $260 \mu\text{g}/\text{m}^3$  over a 24-hour period and  $75 \mu\text{g}/\text{m}^3$  for the annual average (U.S. EPA, 2016). The 1971 secondary standards for TSP were set at  $150 \mu\text{g}/\text{m}^3$  average over a 24-hour period and  $60 \mu\text{g}/\text{m}^3$  for the annual average (U.S. EPA, 2016). In 1987, the EPA set new particulate matter standards, adding regulations for  $\text{PM}_{10}$ . The primary and secondary daily average standard was set at  $150 \mu\text{g}/\text{m}^3$  over a 24-hour period (U.S. EPA, 2017a). In 1997, the EPA once again updated their particulate matter standards, this time adding  $\text{PM}_{2.5}$  standards. The primary and secondary standards were set at  $65 \mu\text{g}/\text{m}^3$  for a 24-hour average and  $15.0 \mu\text{g}/\text{m}^3$  for the annual average (U.S. EPA, 2017a). The addition of the  $\text{PM}_{2.5}$  NAAQS led the Air District to begin monitoring for  $\text{PM}_{2.5}$  in the late 1990's (Tanrikulu et al., 2011). In 2006, the  $\text{PM}_{2.5}$  standards, both primary and secondary, were updated to  $35 \mu\text{g}/\text{m}^3$  for the 24-hour average and the annual average standard remained the same at  $15.0 \mu\text{g}/\text{m}^3$  (U.S. EPA, 2017a). In 2013, the primary standard for the annual average was updated to  $12.0 \mu\text{g}/\text{m}^3$  and the 24-hour primary standard remained at  $35 \mu\text{g}/\text{m}^3$  (U.S. EPA, 2017a). A summary table of NAAQS historical updates are shown in Table 1 below. The NAAQS updates have been the result of studies that were done that showed the harmful effects of particulate matter pollution, and show a constant effort by the EPA to mitigate the impacts of particulate matter pollution.

**Table 1.** Table of historical National Ambient Air Quality Standard updates.

Pollutant	Year Implemented	Averaging Time	National Primary Standard	National Secondary Standard
TSP	1971	24 Hour	260	150
		Annual Mean	75	60
PM10	1987	24 Hour	150	150
PM2.5	1997	24 Hour	65	65
		Annual Mean	15	
	2006	24 Hour	35	35
		Annual Mean	15	
	2013	24 Hour	35	35
		Annual Mean	12	

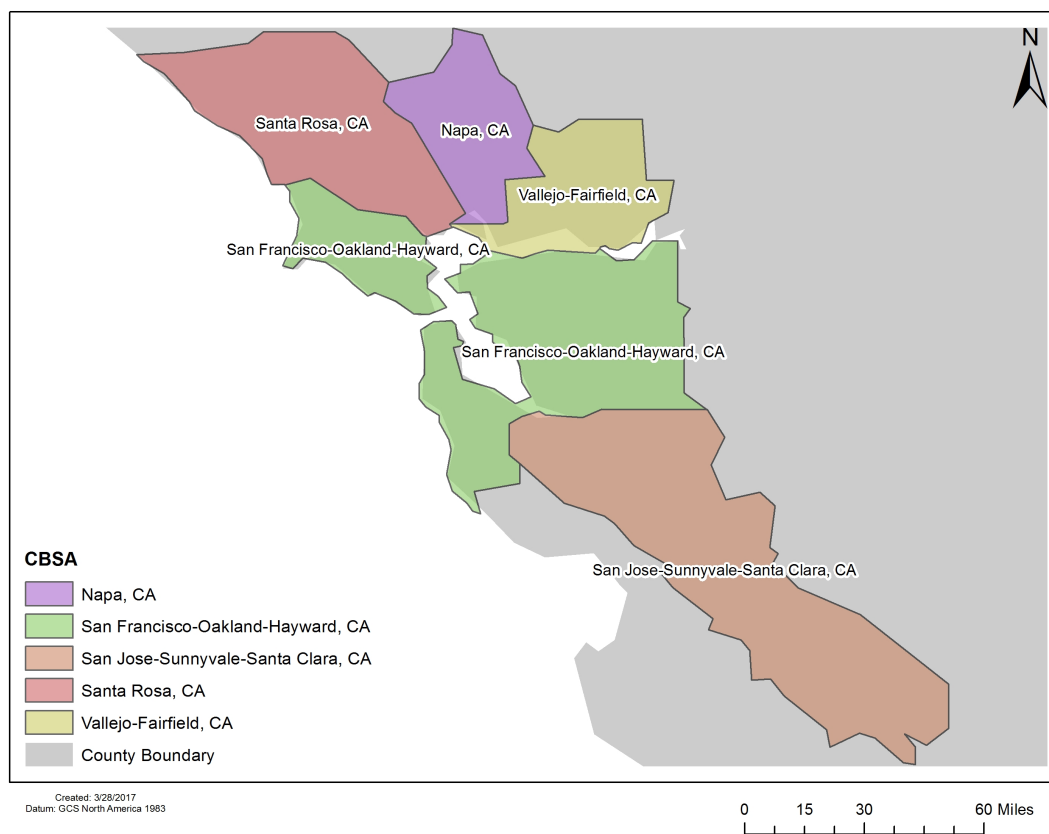
In addition to EPA's NAAQS, air districts located in California need to meet the California Ambient Air Quality Standards (CAAQS). The California Air Resources Board, or CARB, is responsible for setting the CAAQS under the California Health and Safety Code section 39607(e) (California Air Resources Board, 2009). California standards are set to protect public health, and consist of tighter regulations than the NAAQS (California Air Resources Board, 2009). The CAAQS for PM<sub>10</sub> is 20 µg/m<sup>3</sup> for the annual average and 50 µg/m<sup>3</sup> for the 24-hour average (California Air Resources Board, 2009). The CAAQS for PM<sub>2.5</sub> is 12 µg/m<sup>3</sup> for the annual mean, with the same standard for the 24-hour average as the current NAAQS (California Air Resources Board, 2009).

The EPA has guidelines on the number of monitoring stations that should be in a designated area, based on population size and how often the areas exceed the NAAQS (U.S. EPA, 2017c). The designated areas that the EPA uses for determining how many monitoring stations are needed is designated by the U.S. Office of Management and Budget (OMB) and are referred to as core-based statistical areas (CBSAs) and/or metropolitan statistical area (MSA) (U.S. EPA, 2017c). CBSAs are statistical geographic areas where there is at least one urban area with a population over 10,000 (U.S. EPA, 2017c). MSAs are a type of CBSA where the population is greater than 50,000 (U.S. EPA, 2017c). The greater the population, the greater the number of sites per area. In addition to looking at population size for determining the number of sites, the number of sites also depends on how often a CBSA exceeds the NAAQS. If CBSAs exceed the NAAQS, more sites are needed in those areas.

The Air District encompasses nine counties in the San Francisco Bay Area: Alameda, Contra Costa, Marin, Napa, San Francisco, San Mateo, Santa Clara, and the southern part of

Solano and Sonoma counties (Knoderer et al., 2016). The rest of the Solano and Sonoma counties are under the jurisdiction of other air districts. These nine counties are divided into five CBSAs: Napa, San Francisco-Oakland-Hayward, Santa Rosa, San José-Sunnyvale-Santa Clara, and Vallejo-Fairfield (Knoderer et al., 2016). Figure 2 is a map of the CBSAs in the San Francisco Bay Area that are within the jurisdiction of the Air District. Due to population size and how elevated the PM<sub>2.5</sub> levels are, three of the CBSAs are required to have at least one PM<sub>2.5</sub> monitor (Knoderer et al., 2016). The San Francisco-Oakland-Hayward CBSA and San José-Sunnyvale-Santa Clara CBSA are required to have three sites each, and the Napa CBSA needs one site (Knoderer et al., 2016). For PM<sub>10</sub>, the San Francisco-Oakland-Hayward and the San José-Sunnyvale-Santa Clara CBSAs are required to have two to four sites each, while the Santa Rosa, Vallejo-Fairfield, and Napa CBSAs are required to have zero to one site each (Knoderer et al., 2016).

### San Francisco Bay Area Core Based Statistical Areas



**Figure 2.** Map of the CBSAs in the San Francisco Bay Area that are within the jurisdiction of the Bay Area Air Quality Management District.

In addition to meeting the minimum monitoring requirements, the Air District must meet requirements for EPA programs they are participating in. For particulate matter, the programs include National Air Toxics Trends Stations (NATTS), National Core (NCore), and the PM<sub>2.5</sub> Chemical Speciation Network (CSN) (Knoderer et al., 2016). The Air District has one particulate matter NATTS station, located in San José, which is required to monitor lead content in low-volume PM<sub>10</sub> filters (Knoderer et al., 2016). The Air District has one NCore site, at the same location as the NATTS station, which is required to monitor multiple pollutants, including FRM (filter-based) and FEM (BAM) monitoring of PM<sub>2.5</sub> and PM<sub>10-2.5</sub> (Knoderer et al., 2016; U.S. EPA, 2017c). The Air District also has one CSN site, in the same location in San José, which is a filter based monitoring system for PM<sub>2.5</sub> and performs analyses of those filters to characterize the particulates in the ionic form (sodium, potassium, ammonium, nitrate, sulfate and chloride), and also characterizes 36 different types of metals, as well as organic and elemental carbon content (Knoderer et al., 2016). NATTS, NCore, and CSN are programs that the Air District needs to continue monitoring for at this point in time because they are EPA programs that cannot be terminated without special permission.

Aside from the minimum monitoring requirements discussed, the Air District also has monitoring stations for special projects. The Air District has a variety of special purpose monitoring (SPM) stations. An example of a SPM station is a site in the San Geronimo Valley equipped with a black (elemental) carbon analyzer (aethalometer) to monitor how wood smoke contributes to elevated particulate matter levels, specifically when particulates remain stagnant in the air (Knoderer et al., 2016). The Air District hopes that by monitoring in San Geronimo Valley, they can improve efforts to reduce particulate matter levels relating to wood smoke (Knoderer et al., 2016). Special purpose monitors allow for more flexibility, as the Air District does not need special permission to move or close down a site (Knoderer et al., 2016). Additionally, the Air District has a monitoring station for all criteria pollutants, including PM<sub>10</sub> and PM<sub>2.5</sub>, in every county unless a pollutant is in attainment, regardless of whether a pollutant is in attainment or not (Bay Area Air Quality Management District, 2015).

## 2.5. IMPORTANCE OF NETWORK REDESIGN

There are a multitude of reasons why it is important to not only build an effective and accurate air monitoring network, but to also evaluate existing air monitoring networks regularly, and periodically update and redesign the networks as needed. The primary reason is for public health reasons. Another reason for ensuring an air monitoring network is effectively designed is because the data gathered is also used for modeling and meteorological forecasting purposes. Gathering accurate and representative data is crucial in identifying sources of particulates that will aide in the rule development process to mitigate levels of particulates.

### 2.5.1. PUBLIC HEALTH

Particulates can cause health issues, especially for more sensitive groups, including immunocompromised groups such as children and the elderly.  $PM_{10}$  particulates tend to stay in the upper part of the lungs and get filtered out by the body before the particulates reach deep into the lungs.  $PM_{2.5}$  particulates however, travel deeper into the lungs and into the bloodstream. Fine particles can travel into the alveoli and further into the bloodstream (Kumar, 2016). In general, immunocompromised groups such as children and the elderly, particularly those with preexisting respiratory or cardiovascular issues, are more affected by elevated levels of particulates than non-immunocompromised adults.

As one study showed, there is a potential lack of evidence in epidemiological studies of the adverse effects of  $PM_{10-2.5}$  (Ebisu et al., 2016). This study expresses the limitations in studying health impacts from  $PM_{10-2.5}$ , including that the EPA does not monitor for coarse particulates directly, and only calculates  $PM_{10-2.5}$  through the difference between  $PM_{10}$  and  $PM_{2.5}$ , if there are collocated monitors at a site (Ebisu et al., 2016). Another study found similar issues where the studied area did not have particulate matter air monitoring monitors for  $PM_{10}$  and  $PM_{2.5}$  at the same locations (Kumar, 2016). It is difficult and potentially inaccurate to calculate  $PM_{10-2.5}$  concentrations from different locations in an air basin, without data on how the sites correlate with one another. Therefore, it is difficult to understand what the health impacts are strictly from  $PM_{10-2.5}$ . Due to this limitation, there are inconsistencies in health studies from  $PM_{10-2.5}$ . An additional limitation from particulate matter health studies is that many studies have been performed in a single city, which can bias the study (Pope III & Dockery, 2006).



Regardless of limitations regarding the accuracy in determining PM<sub>10-2.5</sub> concentrations, one study found that there was in fact a causal relationship between elevated PM<sub>10-2.5</sub> levels during pregnancy and a lower birth weight (Ebisu et al., 2016). However, another study found that elevated PM<sub>10</sub> concentrations were not directly correlated to birth weight (Kumar, 2016). Yet another study found that increased mortality risks directly correlated to elevated levels of PM<sub>2.5</sub> and sulfur oxide, whereas PM<sub>10-2.5</sub> was not directly linked to elevated mortality risk (Pope III & Dockery, 2006). PM<sub>2.5</sub> studies have shown that infant mortality for all causes, including respiratory and sudden infant death syndrome, were linked to elevated levels of fine particulates (Pope III & Dockery, 2006). There is also a correlation between elevated levels of PM<sub>2.5</sub> with lung cancer, benign respiratory disease and an increased risk of cardiovascular events (Pope III & Dockery, 2006). Fine particulates not only irritate existing respiratory and cardiovascular issues, such as exacerbation of asthma and bronchitis, but can lead to more hospital visits and decrease one's life expectancy (Tanrikulu et al., 2011).

By assessing and making the particulate matter air monitoring network more effective and more representative, the Air District can gather data for a more thorough assessment regarding the effects of PM<sub>10-2.5</sub> and PM<sub>2.5</sub> and how they differ from one another.

## 2.5.2. MODELING, METEOROLOGY AND SOURCE IDENTIFICATION

Another important reason to have an air monitoring network that effectively and accurately collects particulate matter data is for the use of modeling. The Air District uses modeling to perform risk assessment of particulates on the health of residents in the San Francisco Bay Area (Tanrikulu et al., 2011). Modeling has also been used to better understand particulates; their path of travel and how meteorology affects particulate concentration (Tanrikulu et al., 2011). Modeling can also look at trajectories and pollutant transport, which can be used to identify sources (Bermudez et al., 2016).

Source identification a crucial aspect in ensuring an air monitoring network has been properly designed. Understanding what the sources of particulates are allows for the Air District to develop effective rules and programs to help reduce emissions. The collection of representative data is paramount for source identification; having representative data allows for agencies to have fewer sites, as the sites that are operational reflect the concentration of the pollutants of concern for the general area. If there are sites that are right next to pollutant

sources, the data will not reflect what the majority of the population is being exposed to. While it is important to know what sources of pollutants are emitting, it is also important to understand what the general population is being exposed to for a better understanding of health issues related to particulate matter. This is one of the reasons that the Air District characterizes particulate matter for PM<sub>10</sub> and PM<sub>2.5</sub>: to understand the chemical characteristics of particulates, which can be used to identify their sources. For example, black carbon is monitored in the San Geronimo Valley to better understand wood smoke contributions to particulate matter pollution. Once sources can be identified, the Air District can develop regulations that will mitigate particulate matter pollution. For instance, the Air District started a Spare the Air program that banned wood burning on days forecasted to have levels of fine particulates that exceed the NAAQS after it was shown that wood smoke contributed to particulate matter pollution (Bay Area Air Quality Management District, 2015). These programs are essential in mitigating particulate matter pollution.

### 2.5.3. ENVIRONMENTAL EFFECTS

Particulate matter has the ability to affect more than just people's health. Particulates can have significant environmental impacts as well. Particulate matter adversely affect visibility, meteorological rainfall, solar radiation, and cloud formation (Celis et al., 2004; Hong et al., 2002; Srimuruganandam & Shiva Nagendra, 2011). Reduced visibility can contribute to an increase in vehicle accidents (Hassan & Abdel-Aty, 2013). Components of particulates can also lead to the formation of acid rain (Hong et al., 2002). Acid rain is a corrosive result of air pollution (Singh & Agrawal, 2008). Acid rain can deteriorate buildings and cultural landmarks (Agelakopoulou et al., 2009). Particulates are able to scatter and absorb solar radiation, which leads to a temperature increase and acts as a catalyst for ozone formation (Hong et al., 2002). Identifying the sources of emissions that are causing acid rain and reduced visibility is important. These are only a few of the environmental reasons why it is important to monitor particulate matter effectively.

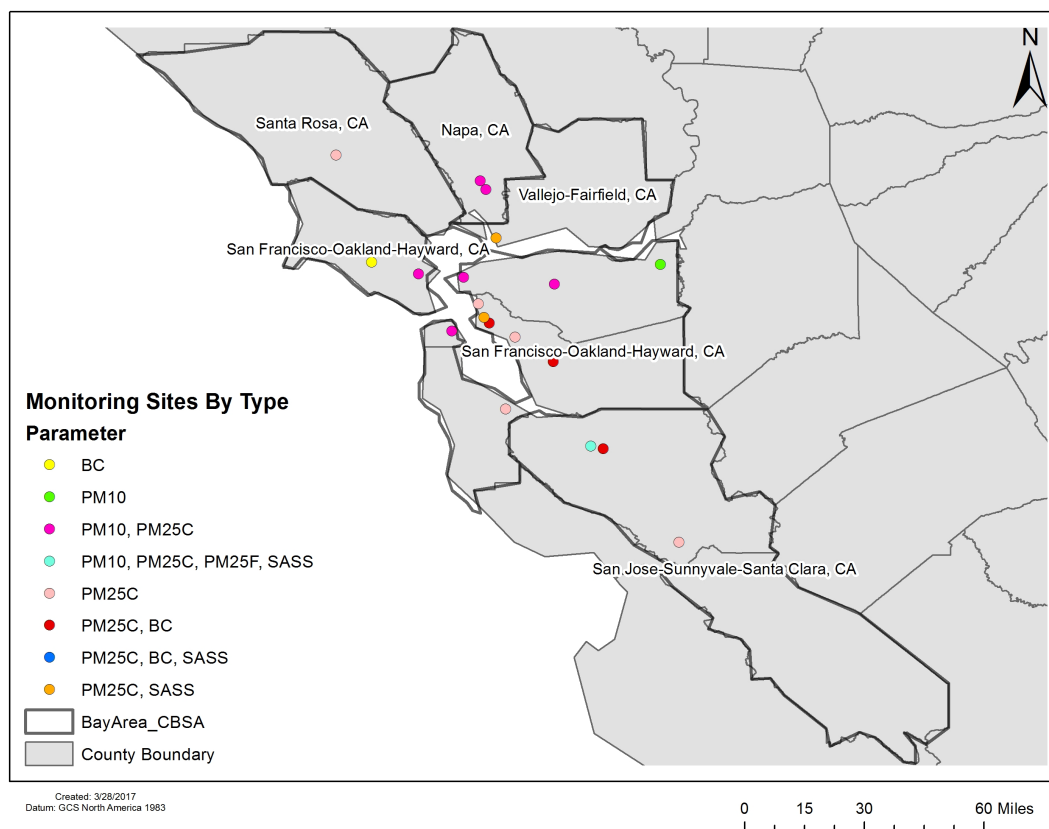
### 3. STUDY AREA

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There are seven types of air monitoring station classifications, as designated by the CFR, that can be applied to particulates monitoring: highest concentration, population exposure, source oriented, general background, regional transport, welfare-related impacts, and quality assurance (Bay Area Air Quality Management District, 2015; U.S. EPA, 2017c). Highest concentration sites are sites that are predicted to have the highest concentration of a pollutant, regardless of population (Bay Area Air Quality Management District, 2015; U.S. EPA, 2017c). Population exposure sites are sites in locations with a high population density (Bay Area Air Quality Management District, 2015; U.S. EPA, 2017c). Source oriented sites are located downwind from major sources of pollutants, such as refineries (Bay Area Air Quality Management District, 2015; U.S. EPA, 2017c). General background sites are located in areas where there are no significant emission sources upwind from the site (Bay Area Air Quality Management District, 2015; U.S. EPA, 2017c). Regional transport sites are located in areas where there is overall higher air pollution, but that are located upwind from sources, and where pollutants may have been transported into the Air District from other air districts (Bay Area Air Quality Management District, 2015; U.S. EPA, 2017c). Welfare-related impact sites are used to monitor for pollutant impacts such as visibility and vegetative damage (Bay Area Air Quality Management District, 2015; U.S. EPA, 2017c). Quality Assurance sites are where there is a secondary instrument, often referred to as a collocated instrument, that is used to confirm that the primary instrument is presenting accurate readings (Bay Area Air Quality Management District, 2015; U.S. EPA, 2017c).

Seven of the Air District's sites will be focused on in this project to compare the chemical composition of both  $PM_{10}$  and  $PM_{2.5}$ . The seven sites include Concord, Livermore, two sites in Oakland designated as Oakland West and Oakland East, San Francisco, San José- Jackson, and San Pablo. In Figure 3, a comprehensive map of  $PM_{10}$  and  $PM_{2.5}$  air monitoring sites is shown.

## San Francisco Bay Area Particulate Matter Air Monitoring Sites



**Figure 3.** Map of particulate matter air monitoring stations in the San Francisco Bay Area.

Each of these sites monitors similar sets of pollutants, but for different reasons. A summary of the sites and what particulate-related monitoring is done at each site can be seen in Table 2.

**Table 2.** List of particulate matter sites in the San Francisco Bay Area used for data analysis.

Site Name	County	Particulates Monitoring
Concord	Contra Costa	Speciated PM <sub>10</sub> , PM <sub>2.5C</sub>
Livermore	Alameda	Speciated PM <sub>2.5</sub> , PM <sub>2.5C</sub> , Aethalometer (BC)
Oakland East	Alameda	PM <sub>2.5C</sub>
Oakland West	Alameda	Speciated PM <sub>2.5</sub> , PM <sub>2.5C</sub> , Aethalometer (BC)
San Francisco	San Francisco	Speciated PM <sub>10</sub> , PM <sub>2.5C</sub>
San José- Jackson	Santa Clara	PM <sub>2.5F</sub> , PM <sub>2.5C</sub> , Low Volume PM <sub>10</sub> , Speciated PM <sub>2.5</sub> , Low Volume PM <sub>10</sub> metals
San Pablo	Contra Costa	Speciated PM <sub>10</sub> , PM <sub>2.5C</sub>

Concord was chosen by the Air District as a site because it is the largest city in Contra

Costa County and the site is located in a valley, with two major freeways (Interstate-680 and CA-4) and two refineries, which makes this area susceptible to trapped pollutants (Knoderer et al., 2016). Livermore was chosen because it is the largest city in the eastern portion of Alameda County and the topography and winds of Livermore can result in elevated levels of PM<sub>2.5</sub> (Knoderer et al., 2016). The sites in Oakland were primarily chosen because Oakland is the largest city in Alameda County, but they also have their unique reasons on why these sites were chosen (Knoderer et al., 2016). Oakland East was chosen as an area-wide representative site because of the large emission sources within its boundaries, including Port of Oakland, Oakland International Airport, and major highways, and high volume of traffic (Knoderer et al., 2016). The Oakland West site was chosen because it is one mile downwind of the Port of Oakland, which is a major source of diesel particulate matter, which has a higher cancer risk. The surrounding community is therefore exposed to a higher concentration of diesel particulate matter than anywhere else in the Bay Area (Knoderer et al., 2016). San Francisco was chosen because it is the second largest city in the Bay Area and the winds can elevate levels of particulate matter due to the number of pollutant sources in San Francisco (Knoderer et al., 2016). In addition, the stagnant air can last multiple days, inversion layers can develop, and high vehicular traffic within the city can all contribute to elevated levels of particulate matter (Knoderer et al., 2016). San José- Jackson was chosen because it is the largest city in the Bay Area and the center of Santa Clara County; it also happens to be the NCore and NATTS site (Knoderer et al., 2016). Additionally, San José-Jackson is surrounded by major highways and an international airport; San José is densely populated and pollutants tend to get blown in from the valley and mix well (Knoderer et al., 2016). San Pablo was chosen because it is the most populated city of the western portion of Contra Costa County, where there is heavy industry, high traffic volumes, two major freeways, close to Chevron Refinery, and downwind from central Bay Area, of which all factors into an area-wide representative site (Knoderer et al., 2016).

There are two types of sites that can affect sampling scheduling and the ease in which a site can be closed or moved: Special Purpose Monitor (SPM) or State or Local Air Monitoring Station (SLAMS). SPM stations are for Air District special projects and are not counted towards minimum monitoring requirements for the EPA, therefore they do not require EPA approval to close the site (Knoderer et al., 2016). SLAMS however, must adhere to EPA's sampling schedule

and are regulated by the EPA, and require approval from EPA to close or change the site (Knoderer et al., 2016). The designation can vary across pollutants at a given site. For example, PM<sub>2.5</sub> monitoring at Concord is a SLAMS, but PM<sub>10</sub> monitoring is SPM, which means PM<sub>10</sub> monitoring can be shut down as the District deems necessary. Whereas the PM<sub>2.5</sub> monitor would need special approval. The Air District needs to request EPA's approval for closing SLAMS monitors. There are different criteria that can be met to demonstrate that closing the monitor will not compromise our ability to demonstrate compliance with the NAAQS. Additionally, the Air District can work with CARB to ensure a monitor closure does not compromise the Air District's ability to demonstrate compliance with the CAAQS. A summary of sites and their designation can be found in Table 3.

**Table 3.** Summary of site type for particulate matter classes at sites studied in San Francisco Bay Area.

<b>Site Name</b>	<b>PM<sub>2.5</sub></b>	<b>PM<sub>2.5</sub> Speciation</b>	<b>PM<sub>10</sub></b>
Concord	SLAMS	n/a	SPM
Livermore	SLAMS	SPM	n/a
Oakland East	SLAMS	n/a	n/a
Oakland West	SLAMS	SPM	n/a
San Francisco	SLAMS	n/a	SPM
San José- Jackson	SLAMS	SLAMS	SLAMS
San Pablo	SLAMS	n/a	SLAMS

## 4. METHODOLOGY

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### 4.1. DATA COLLECTION

The data used for this project was collected from two different databases and Air District servers. The first database used was the Air District's Data Management System (DMS), which was used to collect mass concentration data. PM<sub>10</sub> organic and elemental carbon data from January 1, 2011 to December 31, 2015 was collected from the Air District server. Organic and elemental carbon data and ion data for all of 2015 for PM<sub>2.5</sub> was also collected from an Air District server. The second database was EPA's Air Quality System (AQS) database, which was used to collect ion data, metal content data, and PM<sub>2.5</sub> organic and elemental carbon data from January 1, 2011 to December 31, 2014. The mass concentration data, ionic content data, organic and elemental carbon data collected from AQS, and metals data were all reported in  $\mu\text{g}/\text{m}^3$ . The organic and elemental carbon data that was collected from the Air District was in raw data format and had to be converted into  $\mu\text{g}/\text{m}^3$  using the filter area and air volume passed through the filter. The calculation was done using a formula from the manufacturer's standard operating procedure for the laboratory instrument used to analyze organic and elemental carbon content of particulates on filters (Desert Research Institute, 2005). The calculation can be found below:

$$\text{Formula 2. } \frac{\mu\text{g}}{\text{m}^3} \text{ carbon} = \frac{(\mu\text{g Carbon}/\text{cm}^2)(\text{filter deposit area})}{\text{Air Volume}}$$

Data from 2011-2015 was used for two main reasons: 1.) network assessments are required by the EPA to cover at least five years and 2.) 2011-2015 is the most recent five-year span that has fully approved data (Bay Area Air Quality Management District, 2015; U.S. EPA, 2017c). The CFR requires local air districts to perform a thorough network assessment at least every five years, in addition to air districts' annual network plan (U.S. EPA, 2017c). Analyzing five years' worth of data helps mitigate any bias that could result from abnormal weather events such as severe drought years, wildfires, and abnormally high precipitation. Droughts, wildfires, and precipitation levels all impact particulate matter levels. Droughts and wildfires can result in an increased concentration of particulates in the air, while precipitation can result in a decrease in the concentration of particulates in the air.

There are two different methods of sampling for particulates: continuous monitors and filter based monitors. There are two primary technologies utilized for continuous monitoring of particulates in the San Francisco Bay Area: beta attenuation monitors (BAMs) and

aethalometers. In the San Francisco Bay Area, BAMs are used to monitor PM<sub>2.5</sub> mass concentration and are the Federal Equivalent Method (FEM) for monitoring for particulates. FEMs are approved by the EPA as a corresponding method to monitor for particulate matter mass concentration. BAMs can report down to the one-minute average concentration data, as well as report hourly concentrations. This data is typically used to calculate 24-hour averages, monthly averages, and quarterly averages. Aethalometers are used to analyze black carbon (BC), also known as elemental carbon (EC). Elemental carbon is primarily the result of combustion, biomass burning and electricity and heating units (Briggs & Long, 2016). Data is reported similarly in minute and hourly averages. These instruments are linked to the Air District's Data Management System, which records and reports the data for instantaneous readings. Aethalometers use the transmission of light at a specific wavelength that passes through a non-sampled upon area and the sampled on area and quantifies the concentration of black carbon by calculating the difference (Quincey et al., 2009). The particulate matter size cut fractionator on the inlet can also change, depending on the need of the operator, so both PM<sub>10</sub> and PM<sub>2.5</sub> elemental carbon can be analyzed.

There are three types of filters used for particulate matter analysis: teflon, nylon, and quartz fiber. Teflon filters are used for PM<sub>2.5</sub> and low-volume PM<sub>10</sub> mass concentration analysis, as well as metals content analysis. Nylon filters are used for PM<sub>2.5</sub> ionic composition analysis. Quartz fiber filters are used for PM<sub>2.5</sub> organic and elemental carbon analysis, high volume PM<sub>10</sub> mass concentration analysis, ionic composition analysis, and organic and elemental carbon analysis.

Filter based PM<sub>10</sub> and PM<sub>2.5</sub> sampling are both performed in similar manners. The filter-based method of monitoring for particulate matter mass concentration is the EPA's approved primary method. Air is pulled in through a sampling head that has a specific size cut (PM<sub>10</sub> or PM<sub>2.5</sub>) and is flowed onto a filter for particulates to collect (Noble et al., 2001; U.S. EPA, 2016a). PM<sub>10</sub> filters are sampled on 8" x 10" quartz fiber filters that are placed into filter cassettes on site by field instrument operators prior to their run date (U.S. EPA, 1999). Quartz fiber PM<sub>10</sub> filters are sampled at a high volume (1600-1700 m<sup>3</sup>), over a 24-hour period (midnight to midnight) (U.S. EPA, 1999). PM<sub>2.5</sub> filters for gravimetric analysis are 47mm teflon filters sampled on at a low volume, typically 24 m<sup>3</sup> over a 24-hour period (midnight to midnight) (U.S. EPA, 2016a). For PM<sub>2.5</sub> speciation, there are three different types of filters that are sampled



upon: teflon, nylon and quartz (Met One Instruments, 2001). The analysis is done using Speciation Air Sampling System (SASS) canisters (Met One Instruments, 2001). Each filter has its own individual canister that is placed into an instrument and sampled on for a 24-hour period (midnight to midnight) at an air volume of about  $9.7 \text{ m}^3$  for each filter (Met One Instruments, 2001).

The  $\text{PM}_{10}$  quartz filters are weighed in a temperature and humidity controlled room on an analytical balance before and after sampling (U.S. EPA, 1999, 2017a). The filters are conditioned in the controlled room maintains a temperature range of  $15\text{-}30^\circ\text{C}$  and  $20\text{-}45\%$  relative humidity (%RH) for 24 hours (U.S. EPA, 2017a).  $\text{PM}_{2.5}$  teflon filters are weighed on a microbalance before and after sampling in a temperature controlled room similar to the  $\text{PM}_{10}$  quartz fiber filters, with the exception that the temperature needs to be within  $20\text{-}23^\circ\text{C}$  and  $30\text{-}40\%$  RH (U.S. EPA, 2017a). Ions are analyzed using ion chromatography (IC) (Watson & Chow, 1998). Ion chromatography is performed by the extraction of either nylon or quartz filters in deionized water to remove water-soluble ions from the filter and is run through an ion-exchange column that separates the ions and an electroconductivity detector measures the amount of water soluble ions in the sample (Wilson et al., 2002). Organic and elemental carbon are analyzed using an OC/EC (organic carbon/elemental carbon analyzer), and metals are analyzed using either an X-ray fluorescence (XRF) or an Inductively coupled plasma mass spectrometry (ICP-MS), depending on EPA-approved laboratory analytical methods (Watson & Chow, 1998; Wilson et al., 2002). XRF allows for a relatively quick and non-destructive (the filter is not destroyed in the process of analysis) method for metals analysis in which an x-ray beam is used to measure the amount of metals present on a teflon filter (Wilson et al., 2002). ICP-MS is a destructive analysis, but a more sensitive method for metals analysis, which ionizes the sample using the inductively coupled plasma to analyze what metals are present in the sample (Wilson et al., 2002). An OC/EC functions by heating a section of the quartz filter using helium to  $250^\circ\text{C}$ ,  $500^\circ\text{C}$ ,  $650^\circ\text{C}$ ,  $750^\circ\text{C}$  and  $850^\circ\text{C}$  and using the transmission of a laser through the filter to get a measurement of carbon content (Grover et al., 2009). Organic carbon will volatilize in the  $250\text{-}650^\circ\text{C}$  range, whereas elemental carbon will volatilize in the  $650\text{-}850^\circ\text{C}$  range (Grover et al., 2009). As the organic carbon volatilizes, the carbon is oxidized to carbon dioxide, which then flows through a methanator where the carbon dioxide is reduced to methane, which then passes

through a flame ionization detector (FID) to measure the amount of carbon present (Quincey et al., 2009).

## 4.2. DATA ANALYSIS

A technical data analysis was performed on data downloaded from the two different databases mentioned previously, AQS and the Air District's Data Management System (DMS). The data downloaded from AQS and DMS are the 24-hour averages for each analyte from January 1, 2011 to December 31, 2015. The 24-hour averages were then used to calculate monthly averages to make the datasets more manageable and more representative of concentrations of particulate matter throughout each month. These averages were then used to compare values between methods and to compare whether there is redundancy with site placement or analyses being performed. Averages were also used to determine if there are significant differences between  $PM_{10}$  and  $PM_{2.5}$  values for four sites and if there is some redundancy in monitoring at two different locations in Oakland. Additionally, the chemical composition of the particulates was analyzed to see if there is pollutant source information that can be derived from  $PM_{10}$  chemical speciation that cannot be derived from  $PM_{2.5}$  chemical speciation. Comparison of the chemical speciation data will indicate if chemically speciating both  $PM_{10}$  and  $PM_{2.5}$  filters is necessary for the Air District. Case studies will also be included to understand similarities and differences between chemical components of fine and coarse particulates.

## 5. RESULTS

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### 5.1. INTRODUCTION

Understanding the sources of particulates in the San Francisco Bay is crucial in taking mitigation measures to reduce overall particulates emissions. Studying the chemical components of particulates, both  $PM_{10}$  and  $PM_{2.5}$ , allows regulatory agencies to implement more effective regulations to reduce the concentration of particulates emitted from a given source. To understand sources of fine and coarse particulates, data from the Air District was analyzed to observe the different chemical components of fine and coarse particulates. In addition to data from the Air District, case studies from outside of the San Francisco Bay Area were compared to understand the sources chemical components of particulates and how they differ from  $PM_{10-2.5}$  and  $PM_{2.5}$ . Analyzing the case studies and data from the Air District allows for a better understanding and identification of the primary particulate matter class of concern and how the Air District can better improve the particulate matter air monitoring network in the San Francisco Bay Area.

### 5.2. CASE STUDIES: SOURCES OF PARTICULATES OUTSIDE OF THE SAN FRANCISCO BAY AREA

The coarse particulates in  $PM_{10}$  are often formed from mechanical processes such as construction and re-suspension of road dust and soil (Srimuruganandam & Shiva Nagendra, 2011). These particulates tend to have a high mineral content (Srimuruganandam & Shiva Nagendra, 2011). Another common source of the coarse particulates is sand (Cesari et al., 2016). In one study done in Italy, there was a higher level of the  $PM_{10-2.5}$  during spring and summer seasons with the transport of Saharan Dust (Cesari et al., 2016). In addition to sand, salt from large bodies of water such as the ocean are common contributors of  $PM_{10-2.5}$  (Cesari et al., 2016).

While there are some  $PM_{2.5}$  contributions from sand and sea salt, the contribution is not as significant (Cesari et al., 2016). Fine particulates are often the result of combustion or deposition and incomplete combustion, usually from fossil fuels or biomass (Srimuruganandam & Shiva Nagendra, 2011; Tanrikulu et al., 2011). These fine particulates are often comprised of carbon, sulfates, ammonium and nitrate ions, as well as elements such as arsenic, copper and zinc (Srimuruganandam & Shiva Nagendra, 2011).

PM<sub>10</sub> and PM<sub>2.5</sub> have similar sources in some instances, however industrial and commercial processes contribute more significantly to PM<sub>2.5</sub> emissions than PM<sub>10</sub>, as does combustion, off-road mobile sources, and on-road motor vehicles (Fanai et al., 2014). However, consumer products, dust sources, and fires appear to contribute more to PM<sub>10</sub> than to PM<sub>2.5</sub> emissions (Celis et al., 2004; Fanai et al., 2014). It is unclear, however, how much of the PM<sub>10</sub> emissions in the 2011 Emissions Inventory published by the Air District are part of the coarse aspect of PM<sub>10</sub> or if there is overlap with the fine particulates. It is likely both coarse and fine particulates are components of these different sources of particulates.

In another Italian study, the authors evaluated PM<sub>2.5</sub> chemical composition (trace metals and inorganic ions) to determine sources of PM<sub>2.5</sub> in Treviso, Italy (Squizzato et al., 2017). The study found that the primary sources of PM<sub>2.5</sub> in Treviso were road transport and combustion plants. These sources accounted for 84.1% of PM<sub>2.5</sub> in the province of Treviso, 92.5% in the municipality of Treviso, and 93.5% in Quinto de Treviso (Squizzato et al., 2017). Approximately one third of the mass of PM<sub>2.5</sub> at the Treviso sites were comprised of ammonium, nitrate, and sulfate ions, and elemental sulfur and potassium were the two major metals found in the particulate matter analysis (Squizzato et al., 2017). The authors also found that sodium ions, and elemental iron and manganese increased in concentration during the week, indicating an increase in the number of vehicles on the road (Squizzato et al., 2017). Metals such as iron, manganese, nickel, copper, zinc, titanium, and ionic sodium are associated with wear on brakes and tires (Squizzato et al., 2017). Iron, titanium and manganese metals were found to be the result of non-exhaust emissions from vehicles re-suspended into the atmosphere (Squizzato et al., 2017). Potassium and chloride ions were found to be tracers for wood combustion and biomass burning, with ammonium nitrate and ammonium sulfate were associated with a secondary reaction of a phase change from a gaseous phase to a solid phase (Squizzato et al., 2017). Arsenic, cadmium, and vanadium were found to be associated with industrial emissions from brick and ceramic factories, glass making, non-ferrous metal production, and iron and steel production (Squizzato et al., 2017).

A study performed in the Detroit, Michigan area looked at the effects roadways have on coarse and fine particulates (Oakes et al., 2016). In order to study the particulates, the authors used a PM<sub>10</sub> impactor inlet and an internal impactor to separate the coarse particulates from the fine particulates on two separate filters in order to analyze the two classifications of particulates

individually (Oakes et al., 2016). The authors also monitored particulates at three different distances from the highway of interest: ten meters, 100 meters, and 300 meters from the roadway (Oakes et al., 2016). The authors studied near-road sources of particulates as they believed studying the components of particulates from roadways was crucial in evaluating existing and new control measures to reduce particulates from vehicles (Oakes et al., 2016). Fine particulates can result from the combustion of fuel and lubricating oil, which are seen in higher carbon content and elemental zinc and sulfur (Oakes et al., 2016). Additionally, brakes, tires and re-suspended road particulates contribute to coarse and fine particulates (Oakes et al., 2016). The authors found that elemental sulfur, calcium potassium, iron, zinc, barium, magnesium, copper, manganese, lead, antimony, and titanium were found in both  $PM_{2.5}$  and  $PM_{10-2.5}$ , although calcium, iron and manganese generally had a higher concentration in the coarse particulates and sulfur had a generally higher concentration in fine particulates (Oakes et al., 2016). In general, the authors found that there were sharp decreases in all measured components between ten meters and 100 meters for both  $PM_{10-2.5}$  and  $PM_{2.5}$  (Oakes et al., 2016).

A study performed in Southern California in the South Coast Air Quality Management District jurisdiction (SQAQMD), in which the authors studied coarse particulates and the relationship with trace metals in the Los Angeles Basin (Shirmohammadi et al., 2015). The authors discussed how metals and trace elements were more commonly found in the coarse particulates size range, whereas organic species and secondary ions were found more in fine particulates (Shirmohammadi et al., 2015). As with the Italian and Michigan case studies, the authors note how  $PM_{2.5}$  were the result of combustion and  $PM_{10-2.5}$  were the result of non-exhaust emissions (dust re-suspension, soil, road surface degradation, tires and break wear) (Shirmohammadi et al., 2015). Copper, iron, manganese, zinc, antimony, barium, vanadium, chromium, nickel, and cobalt were observed in coarse particulates in the Los Angeles Air Basin, which are from brake dust and vehicle lubricant (Shirmohammadi et al., 2015). Additionally, sodium, magnesium, sulfur, iron, and calcium were found to be associated with re-suspension of road dust and soil (Shirmohammadi et al., 2015). The authors also discussed how the recent drought in California likely resulted in the increase in the amount of dust and soil on the roadways that can re-suspended into the atmosphere (Shirmohammadi et al., 2015).

In a study performed in Tijuana, Mexico, the author studied the chemical composition of  $PM_{2.5}$  and  $PM_{10-2.5}$  (Minguillón et al., 2014). The authors found that the coarse particulates were

primarily composed of minerals, sea salt, and nitrate (Minguillón et al., 2014). Fine particulates were primarily composed of organic matter, non-sea salt sulfate, and sea salt (Minguillón et al., 2014). In Table 4, the authors of this study listed the correlation between chemical speciation components and the three different classes of particulates: PM<sub>10</sub>, PM<sub>2.5</sub>, and PM<sub>10-2.5</sub>.

**Table 4.** Correlation table of chemical components found in the three different classes of particulate matter in a study performed in Tijuana, Mexico (Minguillón et al., 2014).

Component	PM <sub>10</sub>	PM <sub>2.5</sub>	PM <sub>10-2.5</sub>
Tl	-	-	-
Cs	<b>0.96</b>	-	<b>0.96</b>
NH <sub>4</sub> <sup>+</sup>	<b>0.95</b>	<b>0.95</b>	-
Rb	<b>0.98</b>	0.87	<b>0.97</b>
OC	<b>0.91</b>	<b>0.87</b>	0.48
Se	<b>0.85</b>	<b>0.87</b>	<b>0.82</b>
Na	<b>0.98</b>	<b>0.86</b>	<b>0.89</b>
EC	<b>0.86</b>	<b>0.86</b>	0.01
SO <sub>4</sub> <sup>2-</sup>	<b>0.86</b>	<b>0.86</b>	0.6
Mg	<b>0.97</b>	0.79	<b>0.87</b>
K	<b>0.90</b>	0.75	<b>0.87</b>
Sc	0.65	0.74	0.63
Sr	<b>0.85</b>	0.70	0.77
PM	<b>0.83</b>	0.67	<b>0.84</b>
Ce	<b>0.94</b>	0.66	<b>0.93</b>
Li	<b>0.85</b>	0.65	<b>0.92</b>
V	0.60	0.60	0.54
U	0.51	0.60	-
Fe	<b>0.96</b>	0.53	<b>0.96</b>
La	0.75	0.53	<b>0.81</b>
Cl <sup>-</sup>	<b>0.94</b>	0.52	<b>0.92</b>
Pr	<b>0.92</b>	0.52	<b>0.93</b>
Ba	<b>0.89</b>	0.52	<b>0.85</b>
NO <sub>3</sub> <sup>-</sup>	<b>0.86</b>	0.50	<b>0.91</b>
Th	0.74	0.50	0.61
Nd	<b>0.90</b>	0.49	<b>0.92</b>
Hf	0.56	0.45	0.00
Al <sub>2</sub> O <sub>3</sub>	<b>0.96</b>	0.44	<b>0.96</b>
Ti	<b>0.93</b>	0.42	<b>0.94</b>
Ni	0.28	0.41	0.05
Ca	<b>0.86</b>	0.34	<b>0.87</b>
Zn	0.53	0.32	0.12
Bi	0.34	0.31	0.29
PM	0.75	0.30	0.45
Co	0.80	0.29	<b>0.92</b>
Y	0.65	0.24	0.26
Mn	<b>0.81</b>	0.23	<b>0.95</b>
As	0.16	0.15	0.42
Sb	0.13	0.13	0.06
Sn	0.11	0.12	0.13
Cd	0.10	0.10	0.18
Cr	0.02	0.06	0.01
Zr	0.48	0.04	0.13
W	0.11	0.01	0.11
Pb	0.01	0.00	0.27

The numbers in bold highlight which components have a statistically significant correlation. Comparing the three different columns allows for a better understanding of which chemical components fall within which particulates classification. According to this study, the Tijuana area has a greater concentration of coarse particulates than fine particulates. Elemental and organic carbon are strongly correlated with fine particulates, whereas most of the elemental

metals have been strongly correlated with coarse particulates. Sulfate and ammonium ions are strongly correlated with fine particulates, whereas nitrate and chloride ions are strongly correlated with coarse particulates. Both potassium and magnesium metals can be strongly associated with both coarse and fine particulates, and the authors hypothesize that the reason for this is fine particulates are associated with biomass burning and coarse particulates are linked to mineral content from sand and roadway dust (Minguillón et al., 2014).

The case studies discussed in this section provide a basis for where chemical components of particulate matter,  $PM_{10-2.5}$  and  $PM_{2.5}$ , are derived from. The methodologies of these studies will be used to analyze the data gathered from the San Francisco Bay Area and evaluate what the potential sources of particulates are in the San Francisco Bay Area and the general sources relate to the sources listed in the Air District's 2011 Emissions Inventory. These case studies provide understanding of whether  $PM_{10}$  chemical speciation should still be a priority for the Air District or whether  $PM_{2.5}$  speciation should be a higher priority for the Air District.

### 5.3. SAN FRANCISCO BAY AREA PARTICULATE MATTER DATA

The data from the Air District was broken down into monthly averages from January 2011 to December 2015 for all analytes. The sites were compared for the differences between  $PM_{10}$  and  $PM_{2.5}$  concentrations. Concord, San Francisco, and San Pablo were used to compare high volume  $PM_{10}$  (FRM) monthly average values to  $PM_{2.5}$  (FEM) monthly values for mass concentration. Oakland West and Oakland East were compared for  $PM_{2.5}$  (FEM) to evaluate if there is redundancy in having two Oakland sites. San José-Jackson mass concentration data was used to compare FRM  $PM_{10}$  and FRM  $PM_{2.5}$ , and FRM  $PM_{2.5}$  and FEM  $PM_{2.5}$ . For both ionic content composition and carbon content data, San Pablo ( $PM_{10}$ ) was compared with Oakland West ( $PM_{2.5}$ ) and Concord ( $PM_{10}$ ) was compared with Livermore ( $PM_{2.5}$ ). There isn't a site in the San Francisco Bay Area that have both  $PM_{10}$  and  $PM_{2.5}$  chemical speciation, so sites that had similar wind flow and direction, and were well correlated for FEM  $PM_{2.5}$  were used instead. Correlation graphs were graphed to show if there was a correlation between  $PM_{10}$  and  $PM_{2.5}$  at a given site, and if there is correlation between the two Oakland sites to evaluate if the Air District needs both sites. T-tests will be performed as well to determine if the values are statistically similar. Additionally, correlation graphs were graphed to show if the chemically speciated compounds were correlated between  $PM_{10}$  sites to  $PM_{2.5}$  sites. The goal for performing a

technical data analysis on the particulate matter data from the San Francisco Bay Area is to evaluate if it is a reasonable suggestion to replace the filter-based monitors for PM<sub>10</sub> to continuous monitors to better utilize resources.

### 5.3.1. MASS CONCENTRATION

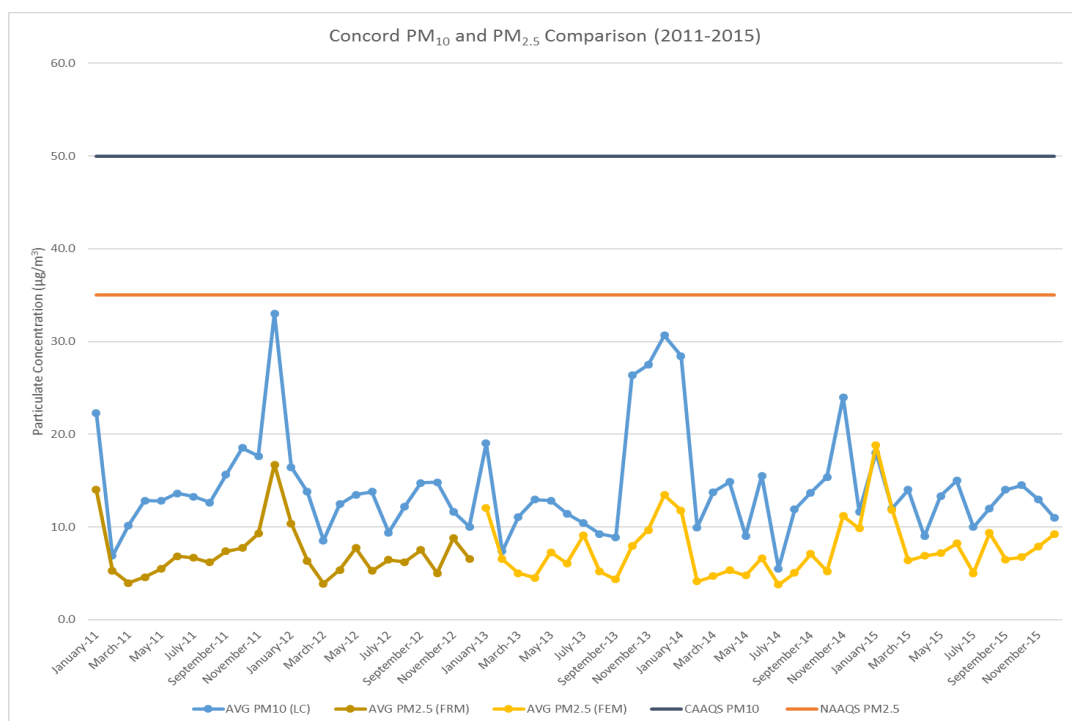
To calculate PM<sub>10-2.5</sub>, the difference between PM<sub>10</sub> and PM<sub>2.5</sub> was calculated, as seen in Formula 3. The Air District does not monitor for PM<sub>10-2.5</sub> directly, and instead uses the concentrations of the low volume PM<sub>10</sub> filters and the PM<sub>2.5</sub> filter to calculate PM<sub>10-2.5</sub>. The only site in the San Francisco Bay Area that PM<sub>10-2.5</sub> is calculated for is the San José- Jackson site. For the purpose of this project, the PM<sub>10-2.5</sub> was calculated for additional sites using the concentrations from the high volume PM<sub>10</sub> filters and the PM<sub>2.5</sub> concentrations from the BAMs. This indirect calculation does include the potential for discrepancies in the calculations because the filter media is not the same from both PM<sub>10</sub> and PM<sub>2.5</sub> and that could allow for some uncertainties.

**Formula 3.**  $PM_{10-2.5} = PM_{10} - PM_{2.5}$

For this section six sites will be compared: Concord, San Francisco, San Pablo, Oakland East, Oakland West, and San José-Jackson. Concord, San Francisco, and San Pablo will be compared to evaluate if the sites need to continue to monitor both PM<sub>10</sub> and PM<sub>2.5</sub>, or at the very least evaluate if it is reasonable to switch to a BAM for PM<sub>10</sub> mass concentration. Two Oakland sites will be evaluated using PM<sub>2.5</sub> BAMs data to evaluate if it is necessary for the Air District to keep both sites. Lastly, San José-Jackson will be evaluated for PM<sub>10-2.5</sub>, PM<sub>2.5</sub> and evaluate if the PM<sub>2.5</sub> FRM and FEM monitors are giving statistically similar results.

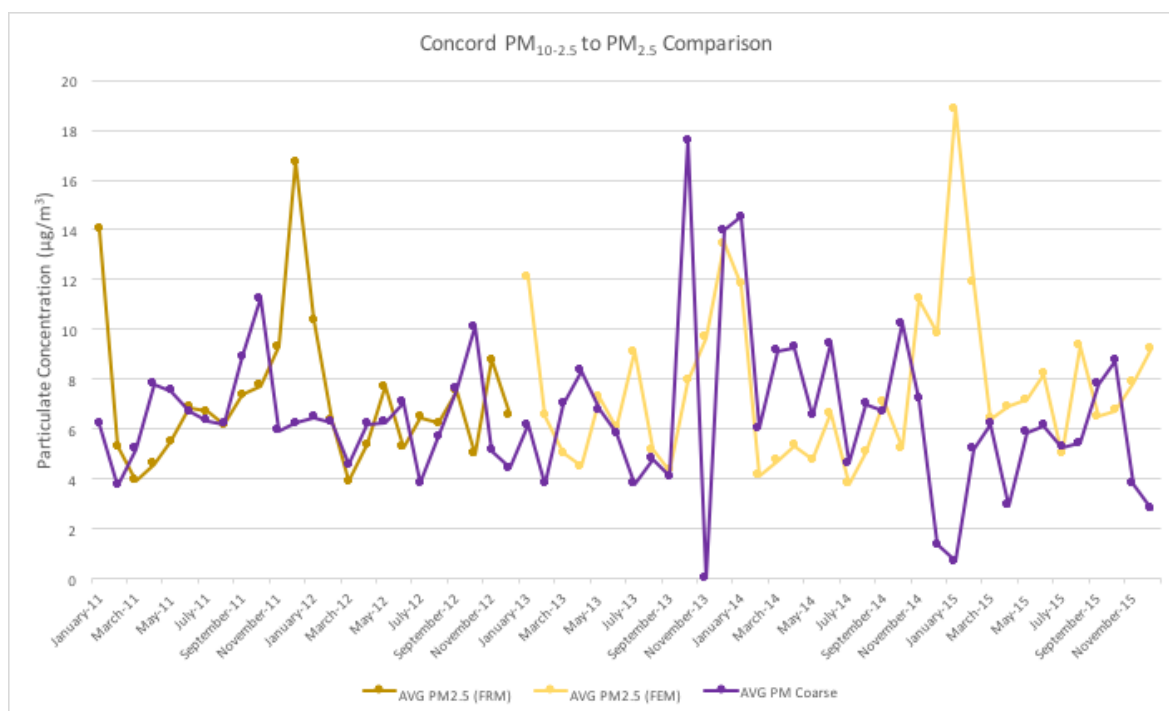
The first, Concord, was evaluated to determine if the site should continue to monitor for PM<sub>10</sub> using the filter-based method (FRM). Concord monitors for PM<sub>10</sub> as a special purpose monitoring station and has a BAM to monitor for PM<sub>2.5</sub>. From January 2011 until the end of 2012, the Air District was using the FRM monitor for PM<sub>2.5</sub> monitoring and switched to a BAM at the beginning of 2013.





**Figure 4.** Comparison of PM<sub>10</sub> and PM<sub>2.5</sub> concentrations at the Concord site in the San Francisco Bay Area from 2011-2015.

In Figure 4, data is graphed to show the general trends of PM<sub>10</sub> and PM<sub>2.5</sub> in relation to each other and the CAAQS for both PM<sub>10</sub> and the NAAQS for PM<sub>2.5</sub>. For both PM<sub>10</sub> and PM<sub>2.5</sub> at Concord the monthly averages were well below both the NAAQS and CAAQS, with the NAAQS for PM<sub>10</sub> being 150 µg/m<sup>3</sup>. The monthly mass concentrations for both PM<sub>10</sub> and PM<sub>2.5</sub> track well with one another. There are a few instances where the PM<sub>2.5</sub> monthly average concentrations are equal to or above the PM<sub>10</sub> monthly average concentrations, and PM<sub>10</sub> concentrations should never be lower than PM<sub>2.5</sub> because PM<sub>10</sub> is partially comprised of PM<sub>2.5</sub>. These discrepancies in the monthly average concentration data could be the result of could be due to the different sampling schedules. The FRM PM<sub>10</sub> sampled every six days through the end of January 2013, and every 12 days from February 2013 onward. The FRM PM<sub>2.5</sub> sampled daily during the winter seasons and every three days the rest of the year until filter-based monitoring for PM<sub>2.5</sub> at Concord ended in December 2012. FEM PM<sub>2.5</sub> monitoring sampled daily from January 2013 and onward. Due to the sampling schedule of PM<sub>10</sub> filters, there are some months where there was only one valid PM<sub>10</sub> filter. Comparing different sets of data that have different sampling frequencies can skew the data.

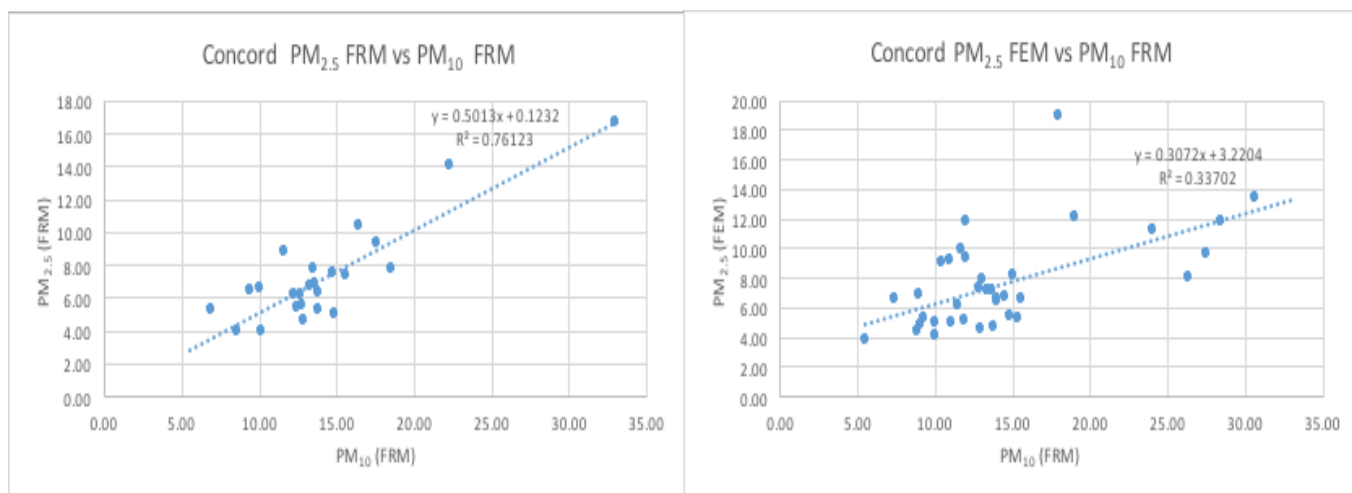


**Figure 5.** Comparison of PM<sub>10-2.5</sub> and PM<sub>2.5</sub> concentrations at the Concord site in the San Francisco Bay Area from 2011-2015.

In Figure 5, the concentrations of PM<sub>10-2.5</sub> and PM<sub>2.5</sub> are compared. The time series graphs show that for most of the five-year period PM<sub>10-2.5</sub> are around the same concentrations. The exceptions are during the winter seasons, where three of the four winters had higher PM<sub>2.5</sub> monthly averages than PM<sub>10-2.5</sub>, and during the one other winter the PM<sub>10-2.5</sub> has a higher monthly average concentration than PM<sub>2.5</sub>. The beginning half of 2015-2016 winter season shows that the PM<sub>2.5</sub> concentrations were higher than the PM<sub>10</sub> concentrations. The dramatic drop in the PM<sub>10-2.5</sub> monthly average in November 2013 is likely due to the availability of PM<sub>10</sub> data due to the sampling schedule of the filter-based monitoring.

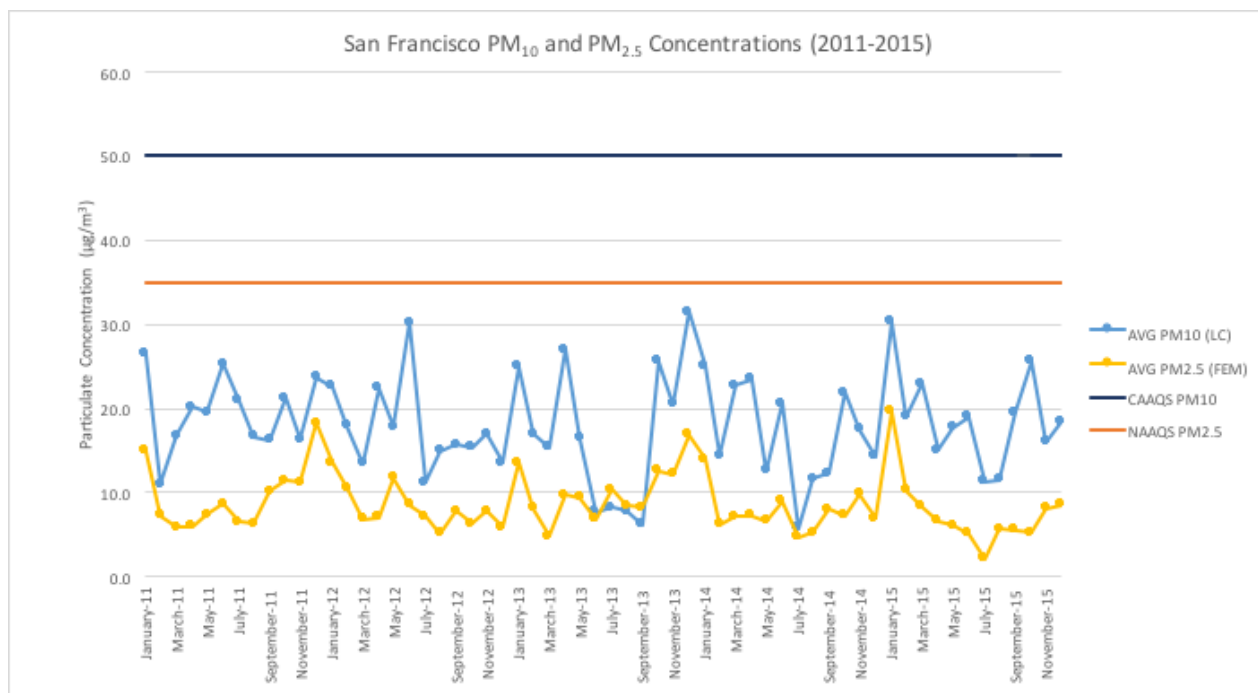
In Figure 6, the two graphs show the correlation graphs comparing FRM with the corresponding BAM data and the FEM with the corresponding BAM data. The correlation graph comparing the FRM (PM<sub>10</sub>) and the BAM (PM<sub>2.5</sub>) results show that there is a good correlation between the datasets with a correlation coefficient of 0.76. However, the correlation data for the FEM (PM<sub>10</sub>) and BAM (PM<sub>2.5</sub>) data shows that there is not a good correlation between these two data sets, with a correlation coefficient of 0.34. The correlation could be the result of the different methods of sampling and the different size cuts of particulate matter, PM<sub>10</sub> versus PM<sub>2.5</sub>. The poor correlation could be the result of an outlier. For future analyses, statistical

outliers should be tested for an excluded. Additionally, it can be observed that when  $PM_{10}$  increases in concentration,  $PM_{2.5}$  does as well, and in some instances  $PM_{10}$  is almost equal or equal to  $PM_{2.5}$  concentrations. The two different correlation values show that it is difficult to compare the values across two analysis methods for two different classes of particulates ( $PM_{10}$  and  $PM_{2.5}$ ). It is possible that if the Air District switches to a BAM for  $PM_{10}$  monitoring, the correlation would be better than the correlation for FRM of  $PM_{10}$  versus BAM  $PM_{2.5}$ .



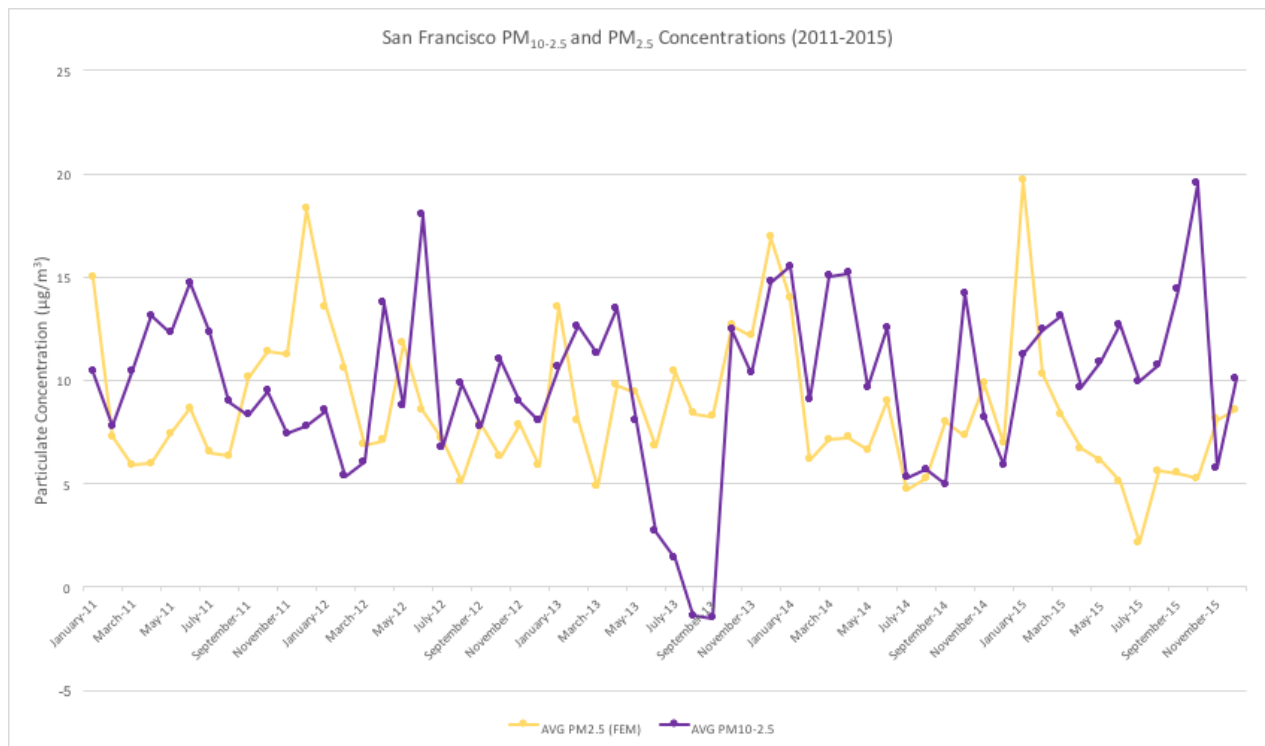
**Figure 6.** Correlation graphs of Concord particulate matter data for both the FRM and FEM methods of  $PM_{2.5}$  versus corresponding FRM  $PM_{10}$  data.

The next site that will be discussed is San Francisco, comparing  $PM_{10}$  FRM and  $PM_{2.5}$  BAM. In Figure 7, the monthly average concentrations of  $PM_{10}$  are graphed along with the monthly averages of  $PM_{2.5}$  in relation to each other and the CAAQS for  $PM_{10}$  and the NAAQS  $PM_{2.5}$ . For both  $PM_{10}$  and  $PM_{2.5}$  the monthly averages were well below both the NAAQS and CAAQS, with the NAAQS for  $PM_{10}$  being  $150 \mu\text{g}/\text{m}^3$ . There are instances where the  $PM_{10}$  concentrations are not significantly higher than  $PM_{2.5}$ .



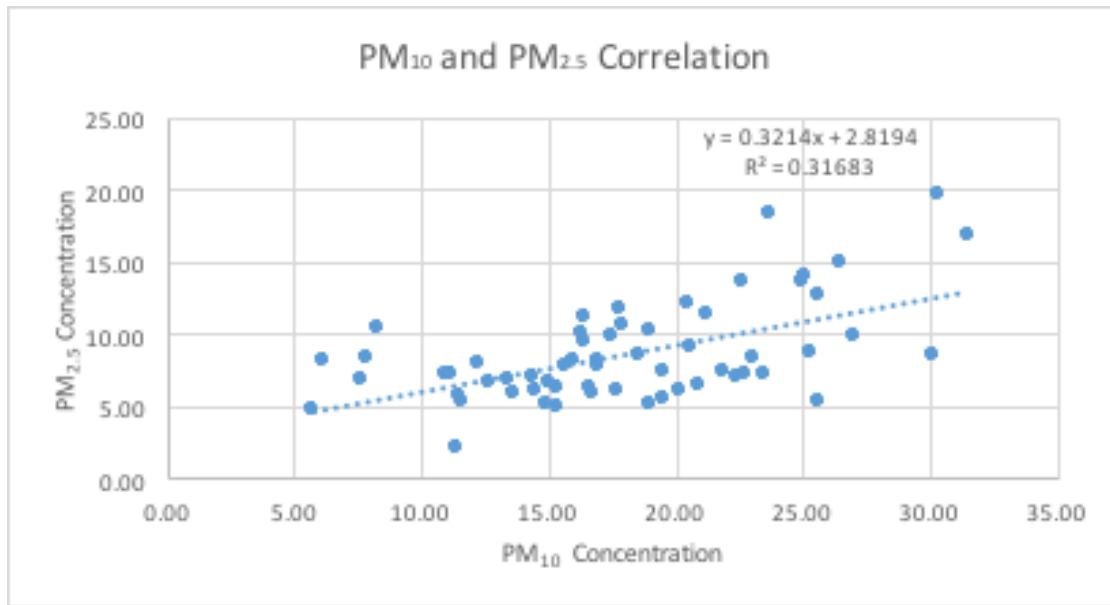
**Figure 7.** Comparison of PM<sub>10</sub> and PM<sub>2.5</sub> concentrations at the San Francisco site in the San Francisco Bay Area from 2011-2015.

In Figure 8, the concentrations on PM<sub>10-2.5</sub> and PM<sub>2.5</sub> were graphed for San Francisco from 2011-2015. The comparison shows that there was some seasonal variability where one class of particulates was higher than the other by a larger margin than the rest of the year. However, the numbers are very similar outside of the seasonal variabilities. The drastic drop in PM<sub>10-2.5</sub> monthly average concentration during September and October 2013 are likely due to the lack of available data during those months due to the sampling schedule for PM<sub>10</sub> filter-based monitoring.



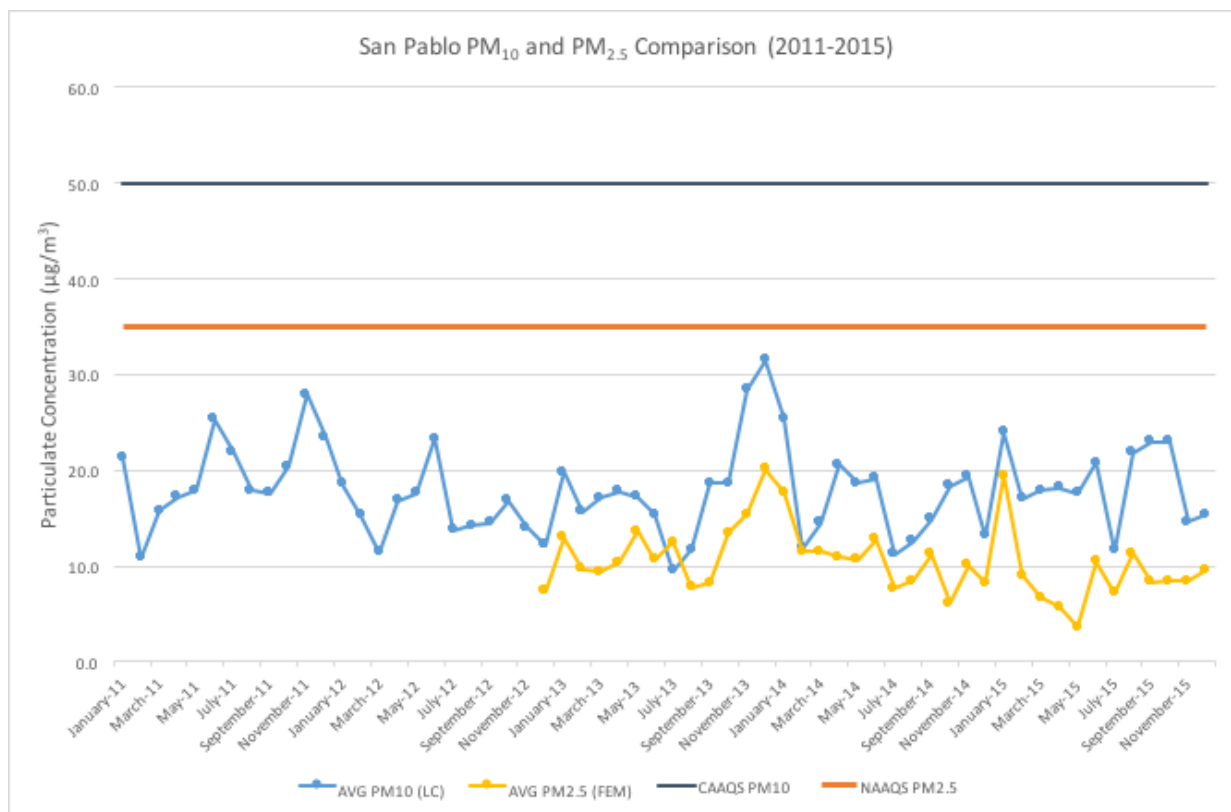
**Figure 8.** Comparison of  $PM_{10-2.5}$  and  $PM_{2.5}$  concentrations at the San Francisco site in the San Francisco Bay Area from 2011-2015.

In Figure 9, the correlation graph has been charted. The correlation coefficient for  $PM_{10}$  FRM against the  $PM_{2.5}$  BAM data is 0.32. These results could once again be due to comparing a filter-based  $PM_{10}$  dataset with a  $PM_{2.5}$  BAM dataset. However, there are some discrepancies, as there are instances where  $PM_{2.5}$  averages are higher than  $PM_{10}$  averages. Having higher  $PM_{2.5}$  concentration than  $PM_{10}$  should be impossible, as  $PM_{10}$  would include all particulates in  $PM_{2.5}$ . The discrepancies could be the result of having too few  $PM_{10}$  data points for those months, which would bias the monthly averages. This could also be due to the differences in sampling methods and comparing different types of sampling methods across different types of particulate matter classes could indicate data is not statistically similar when it could be.

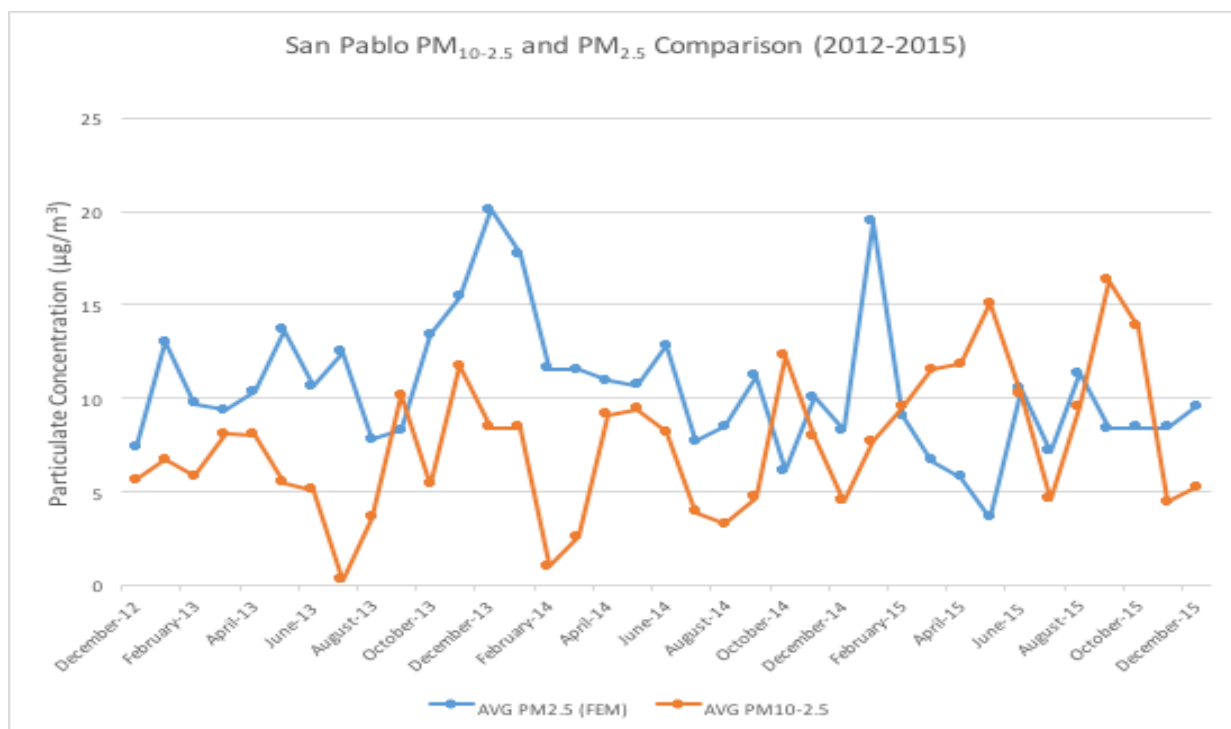


**Figure 9.** Correlation graphs of San Francisco particulate matter data for both the FRM and FEM methods versus corresponding BAMs data.

The next site that will be evaluated is San Pablo. San Pablo has a  $PM_{10}$  FRM and  $PM_{2.5}$  BAM, which will be analyzed. San Pablo started monitoring for  $PM_{2.5}$  using a BAM in December 2012. In Figure 10, the monthly average concentrations of  $PM_{10}$  are graphed along with the monthly averages of  $PM_{2.5}$  in relation to each other and the CAAQS for  $PM_{10}$  and the NAAQS for  $PM_{2.5}$ . For both  $PM_{10}$  and  $PM_{2.5}$  the monthly averages were well below both the NAAQS and CAAQS, with the NAAQS for  $PM_{10}$  being  $150 \mu\text{g}/\text{m}^3$ . Additionally, Figure 11 shows the relationship between  $PM_{10-2.5}$  and  $PM_{2.5}$ . This time series graph shows how for most of the two-year span of data,  $PM_{2.5}$  was present in larger concentrations than  $PM_{10-2.5}$ . This data indicates that fine particulates are more prevalent at the San Pablo site than coarse particulates. There are also seasonal variabilities in  $PM_{2.5}$  concentrations during the winter months of the studied period. The elevated  $PM_{2.5}$  values could indicate that the weather or the habits of the surrounding population contributes more to  $PM_{2.5}$  in the winter months, such as wood burning as a source of heat.

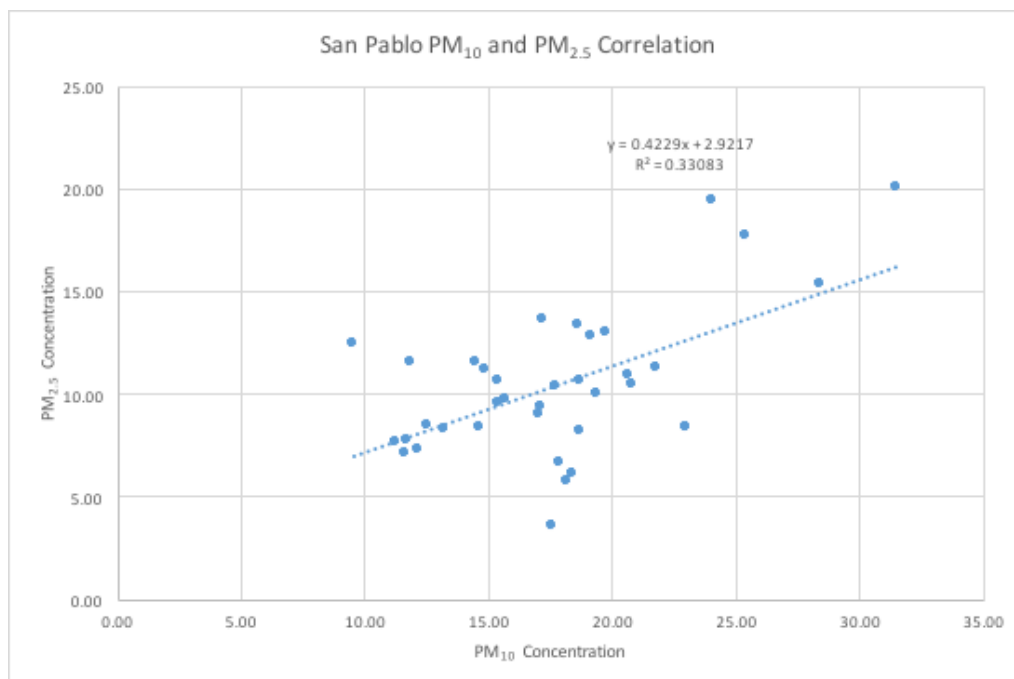


**Figure 10.** Comparison of PM<sub>10</sub> and PM<sub>2.5</sub> concentrations at the San Pablo site in the San Francisco Bay Area from 2011-2015.



**Figure 11.** Comparison of PM<sub>10-2.5</sub> and PM<sub>2.5</sub> concentrations at the San Pablo site in the San Francisco Bay Area from December 2012-2015.

In addition, the correlation graph (Figure 12) was plotted comparing the PM<sub>10</sub> FRM and PM<sub>2.5</sub> BAM datasets. The correlation coefficient was 0.33. A correlation coefficient this low indicates a poor correlation between the two datasets.

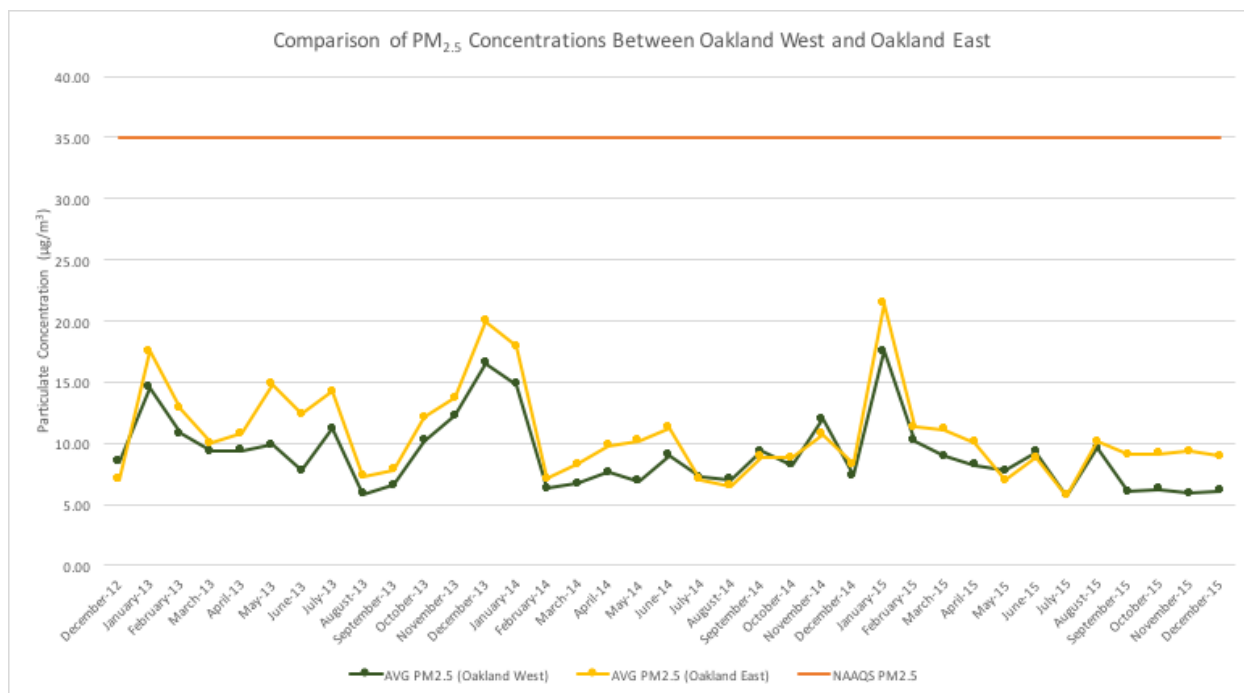


**Figure 12.** Correlation graphs of San Pablo particulate matter data for both the FRM and FEM methods versus corresponding BAMs data.

There are some discrepancies in the datasets that could have impacted the correlation coefficient. There are some instances where the PM<sub>2.5</sub> concentrations are larger than the PM<sub>10</sub> concentrations, which shouldn't be true. And once again, the differences in sampling methods and comparing different types of sampling methods across different types of particulate matter classes could allow for these discrepancies. The data shows that at the San Pablo site, there trend appears to be that PM<sub>2.5</sub> is present more often than the coarse particulates PM<sub>10-2.5</sub>.

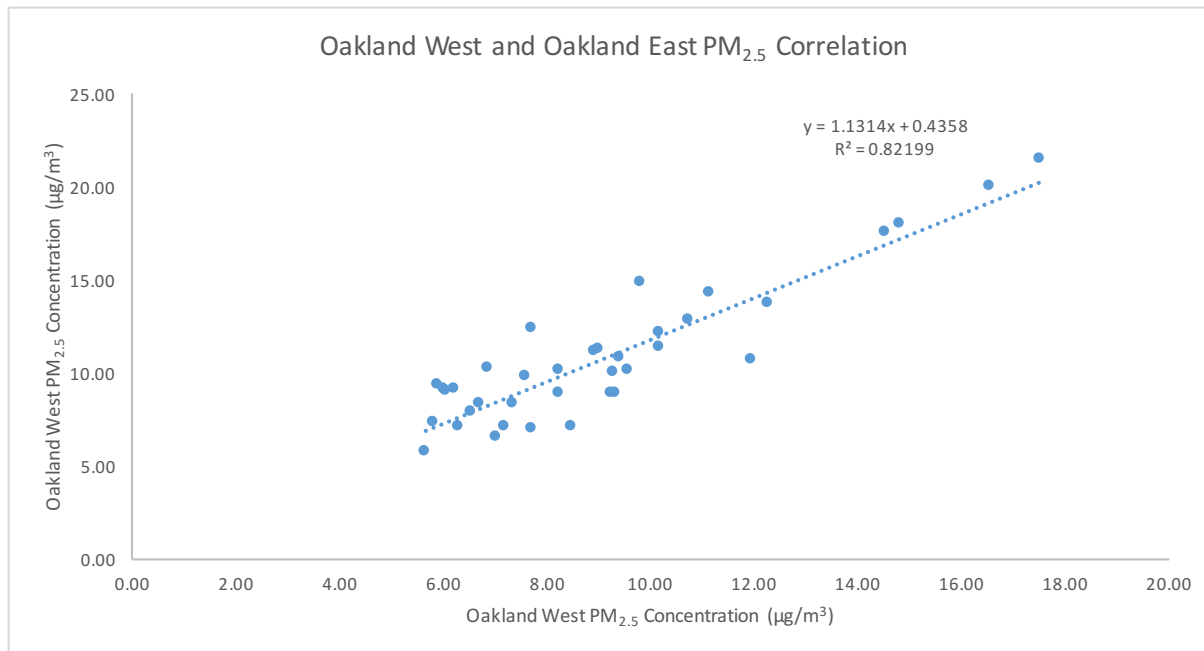
The next mass concentration comparison is of two Oakland sites, Oakland West and Oakland East, where the PM<sub>2.5</sub> BAMs data for the two sites will be compared to evaluate if both sites are needed. Both Oakland sites have BAMs in place, however Oakland East only started monitoring for PM<sub>2.5</sub> in December 2012. In Figure 13, the BAMs PM<sub>2.5</sub> data was plotted in relation to the 24-hour NAAQS for PM<sub>2.5</sub>. The graph indicates that the averages are almost the same in most instances.





**Figure 13.** Comparison of FRM PM<sub>2.5</sub> at Oakland West and Oakland East sites in the San Francisco Bay Area.

In addition to the time-series graph, a correlation graph was plotted in Figure 14. The correlation coefficient for the two datasets is 0.82, indicating that there is a good correlation between the two datasets. The t-test results indicate that the two datasets for the Oakland West and Oakland East sites are statistically similar. The two sides of the t-test are statistically similar at 1% significance and the p-value fails to reject the null hypothesis. These results indicate that monitoring in both locations is unnecessary as the two sites are not only well correlated, but they are also statistically similar.



**Figure 14.** Correlation graph of PM<sub>2.5</sub> FEM BAMs at Oakland West and Oakland East.

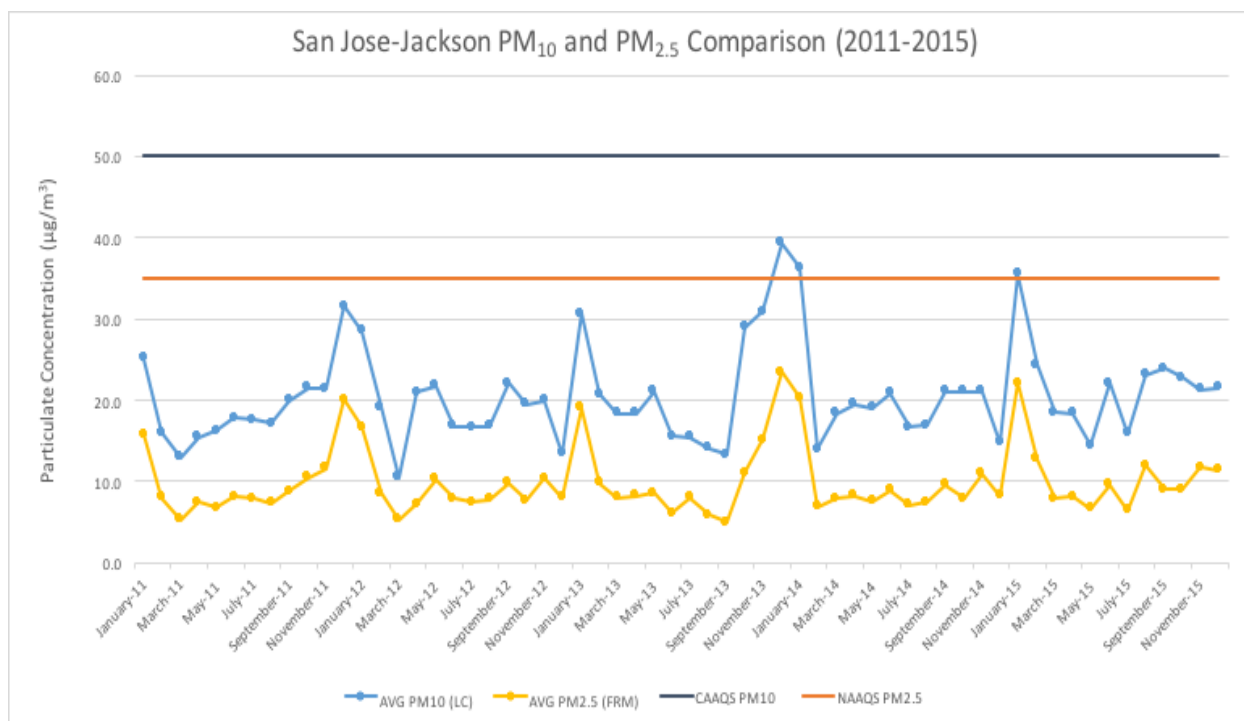
**Table 5.** T-test results for the FEM BAMs for PM<sub>2.5</sub> at the two Oakland sites.

	<i>Variable 1</i>	<i>Variable 2</i>
Mean	9.10	10.73
Variance	8.89	13.85
Observations	37	37
Hypothesized Mean Difference	0	
df	69	
t Stat	-2.08	
P(T<=t) one-tail	0.02	
t Critical one-tail	1.67	
P(T<=t) two-tail	0.04	
t Critical two-tail	1.99	

The final mass concentration site that will be analyzed is San José- Jackson. San José- Jackson monitors PM<sub>10</sub> (FRM) and PM<sub>2.5</sub> (FRM and FEM), except the PM<sub>10</sub> is sampled at a low volume instead of a high volume, and is sampled on the same type of filter as the FRM PM<sub>2.5</sub>. The purpose of this analysis is to analyze whether the FRM and FEM methods are comparable at San José- Jackson and compare whether monitoring both PM<sub>10</sub> and PM<sub>2.5</sub> is necessary at San José-Jackson.

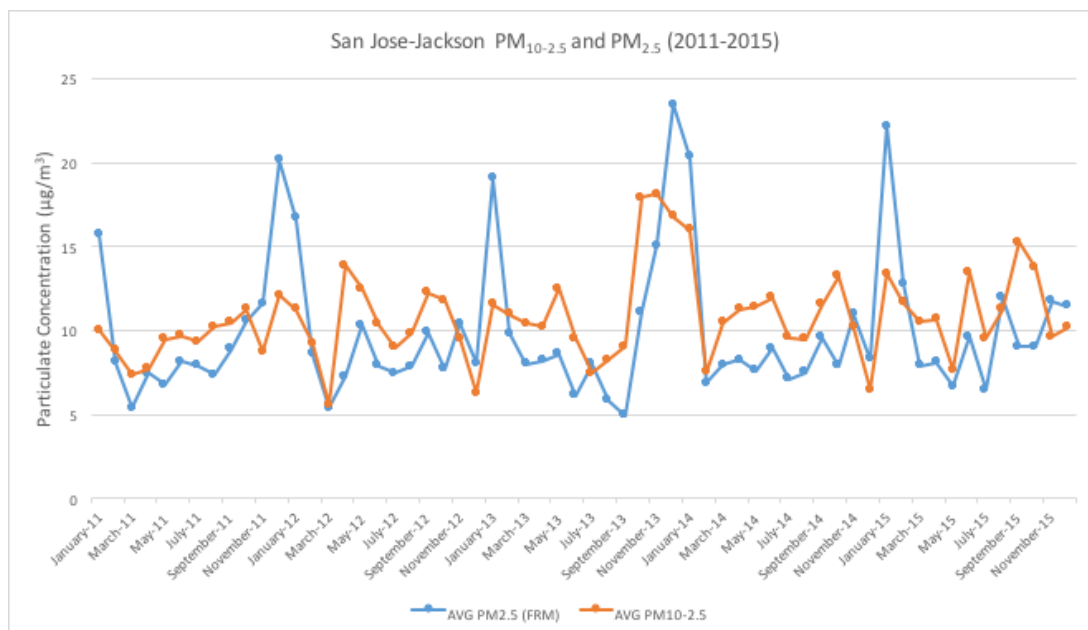
In Figure 15, FRM PM<sub>10</sub> and FRM PM<sub>2.5</sub> were graphed in a time series plot to observe trends and similarities between the two datasets in comparison with the NAAQS for PM<sub>2.5</sub> and

CAAQS for PM<sub>10</sub>. FRM PM<sub>2.5</sub> concentrations are well below the 24-hour NAAQS. Additionally, the FRM PM<sub>10</sub> averages are well below the 24-hour NAAQS, and are below the 24-hour CAAQS. Both indicating that the Air District has the particulate matter concentrations under control.



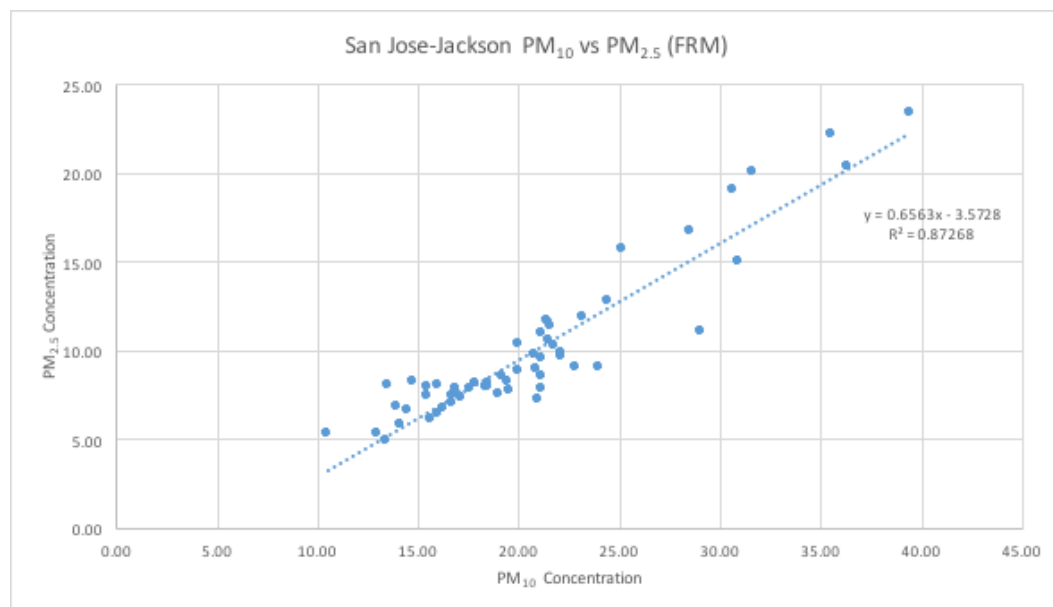
**Figure 15.** Comparison of PM<sub>10</sub> and PM<sub>2.5</sub> concentrations at the San José- Jackson site in the San Francisco Bay Area from 2011-2015.

In Figure 16, the monthly PM<sub>10-2.5</sub> and PM<sub>2.5</sub> monthly averages were plotted to analyze the variability between the two species. The concentrations of PM<sub>10-2.5</sub> and PM<sub>2.5</sub> are similar throughout most of the years during the 2011-2015 period, with the exception of the winter seasons. For all the winter seasons during this time, PM<sub>2.5</sub> significantly spikes higher than the PM<sub>10-2.5</sub> concentrations. These results indicate a seasonal shift in PM<sub>2.5</sub> concentrations that could be due to meteorological factors (temperature, wind speed and direction, inversion layers) and habits of the population in the surrounding area, such as burning more firewood during the winter months.



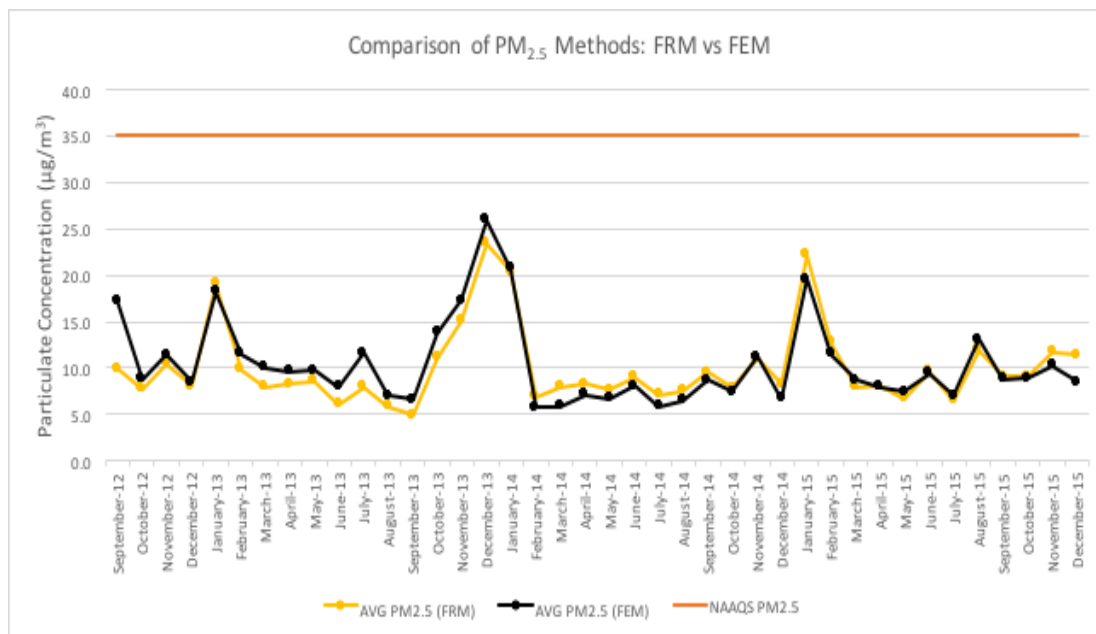
**Figure 16.** Comparison of  $PM_{10-2.5}$  and  $PM_{2.5}$  concentrations at the San José- Jackson site in the San Francisco Bay Area from 2011-2015.

In addition to the time-series plots, a correlation graph was plotted (Figure 17) to analyze if  $PM_{10}$  and  $PM_{2.5}$  were correlated. The correlation coefficient from the graph is 0.87. The correlation coefficient indicates that  $PM_{10}$  and  $PM_{2.5}$  concentrations during the studied period have a strong positive correlation.



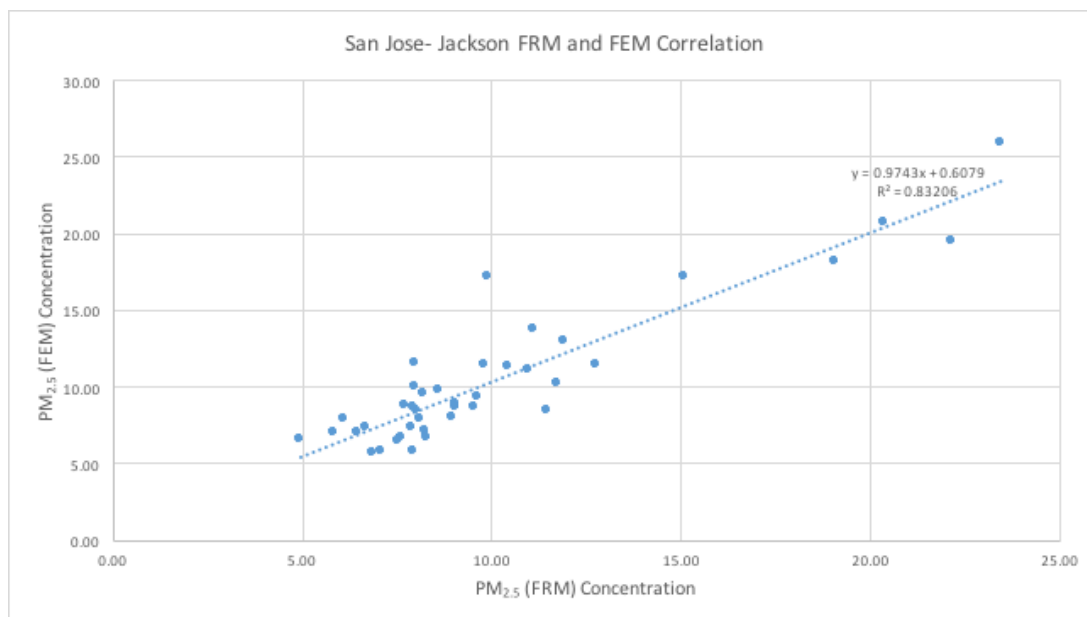
**Figure 17.** Correlation graph between FRM  $PM_{10}$  and FRM  $PM_{2.5}$  for San José-Jackson.

The FRM and FEM monitoring techniques for PM<sub>2.5</sub> were also compared. Figure 18 shows that the FRM PM<sub>2.5</sub> and FEM PM<sub>2.5</sub> methods of monitoring are similar and almost the same over the period of September 2012 until the end of 2015, when both monitors were operational. In addition to the time series graph, a correlation plot was also done.



**Figure 18.** Comparison of FRM and FEM monitoring techniques for PM<sub>2.5</sub> at San José-Jackson site in the San Francisco Bay Area.

The correlation graph in Figure 19, the correlation coefficient was 0.83, which indicates a strong positive correlation between the values for FRM PM<sub>2.5</sub> and FEM PM<sub>2.5</sub>. The slope of the regression analysis is close to one, which also indicates a strong correlation between the two data sets. Additionally, the t-test was performed for the PM<sub>2.5</sub> FRM and FEM analysis, as seen in Table 6. The t-test indicates that the two datasets for the PM<sub>2.5</sub> FRM and FEM comparison are statistically similar. The two sides of the t-test are statistically similar at 1% significance and the p-value fails to reject the null hypothesis ( $P > 1\%$ ). The results of the correlation graph and t-test agree with the literature that has been reviewed in this paper. The FRM and FEM results for PM<sub>2.5</sub> have statistically similar results, indicating that the two methods can be accurately used for the monitoring of PM<sub>2.5</sub>.



**Figure 19.** Correlation graph between FRM PM<sub>2.5</sub> and FEM PM<sub>2.5</sub> for San José-Jackson.

**Table 6.** T-test results for FEM PM<sub>2.5</sub> and FRM PM<sub>2.5</sub> at San José-Jackson.

	<i>Variable</i> <i>1</i>	<i>Variable</i> <i>2</i>
Mean	10.05	10.40
Variance	18.54	21.15
Observations	40	40
Hypothesized Mean Difference	0	
df	78	
t Stat	-0.35	
P(T<=t) one-tail	0.36	
t Critical one-tail	1.66	
P(T<=t) two-tail	0.73	
t Critical two-tail	1.99	

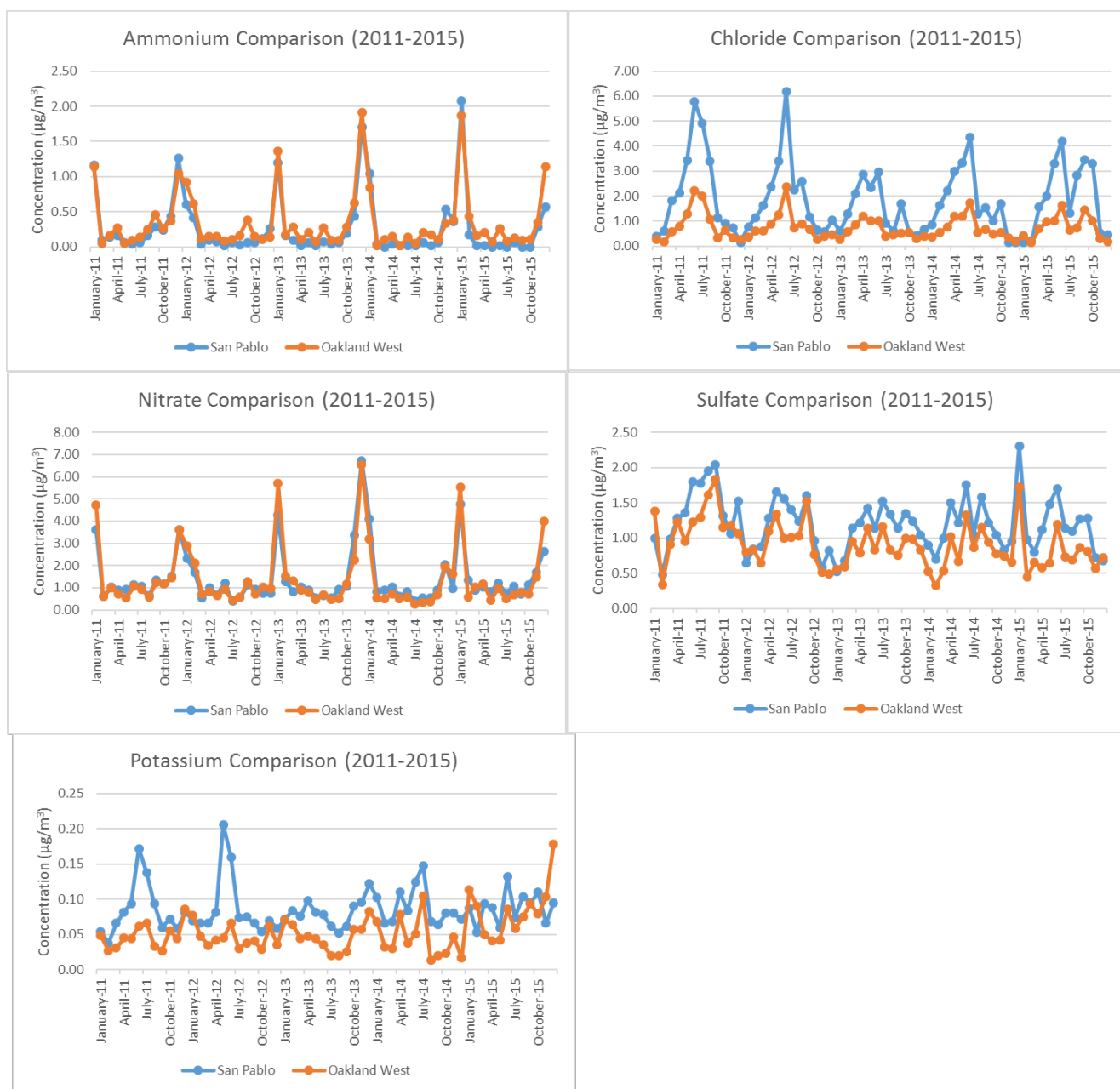
The results from the mass concentration datasets across the six sites vary. PM<sub>10-2.5</sub> concentrations and PM<sub>2.5</sub> concentrations have similar concentrations across the five-year period for the studied sites, with winter seasonally increases in PM<sub>2.5</sub> concentrations likely due to a combination of vehicle emissions, wood smoke, and meteorological effects such as inversion layers, and wind speed and direction. Comparing the two Oakland sites indicates that both sites are not needed. The concentrations for PM<sub>2.5</sub> are statistically similar and well correlated. San José-Jackson results indicated that PM<sub>10</sub> and PM<sub>2.5</sub> that the FRM and FEM results are statistically similar as well, indicating that it is acceptable to use BAMs to monitor for PM<sub>2.5</sub> in place of filters, which is in agreement with EPA's judgment on the use of BAMs. This can also

indicate that BAMs can be used to monitor for  $PM_{10}$ . Additionally, literature supports the use of BAMs for  $PM_{10}$  monitoring, as the concentrations are in agreement. South Coast Air Quality Management District also uses BAMs to monitor for  $PM_{10}$  mass concentration.

### 5.3.2. ION COMPOSITION

Analysis of particulate matter composition is crucial in understanding sources of particulate matter. First, ionic composition was analyzed. The first pair to be analyzed was San Pablo and Oakland West. The second pair to be analyzed was Concord and Livermore. Unfortunately, the Air District does not have a  $PM_{10}$  and  $PM_{2.5}$  chemical speciation monitor at the same sites. The two pairs of sites were chosen because the  $PM_{2.5}$  correlation coefficient values were high and sites were chosen for the best possible pairings. Additionally, there may have been other pairings that had a better correlation coefficient, in discussing the issue with the Supervising Air Quality Meteorologist at the Air District, it made more sense to compare Oakland West and San Pablo because wind flow and direction made it so these two sites were more comparable. The ions to be compared are ammonium, chloride, nitrate, sulfate, and potassium.  $PM_{2.5}$  chemical speciation also analyzes for sodium.  $PM_{10}$  chemical speciation does not analyze for sodium because at a high-volume sampling, the sodium concentration is high enough to cause issues in quantification of the data. The San Francisco Bay Area has a large source of sodium because of the Pacific Ocean and the San Francisco Bay and can interfere with sodium analysis because of the proximity to all the Air District's sites.

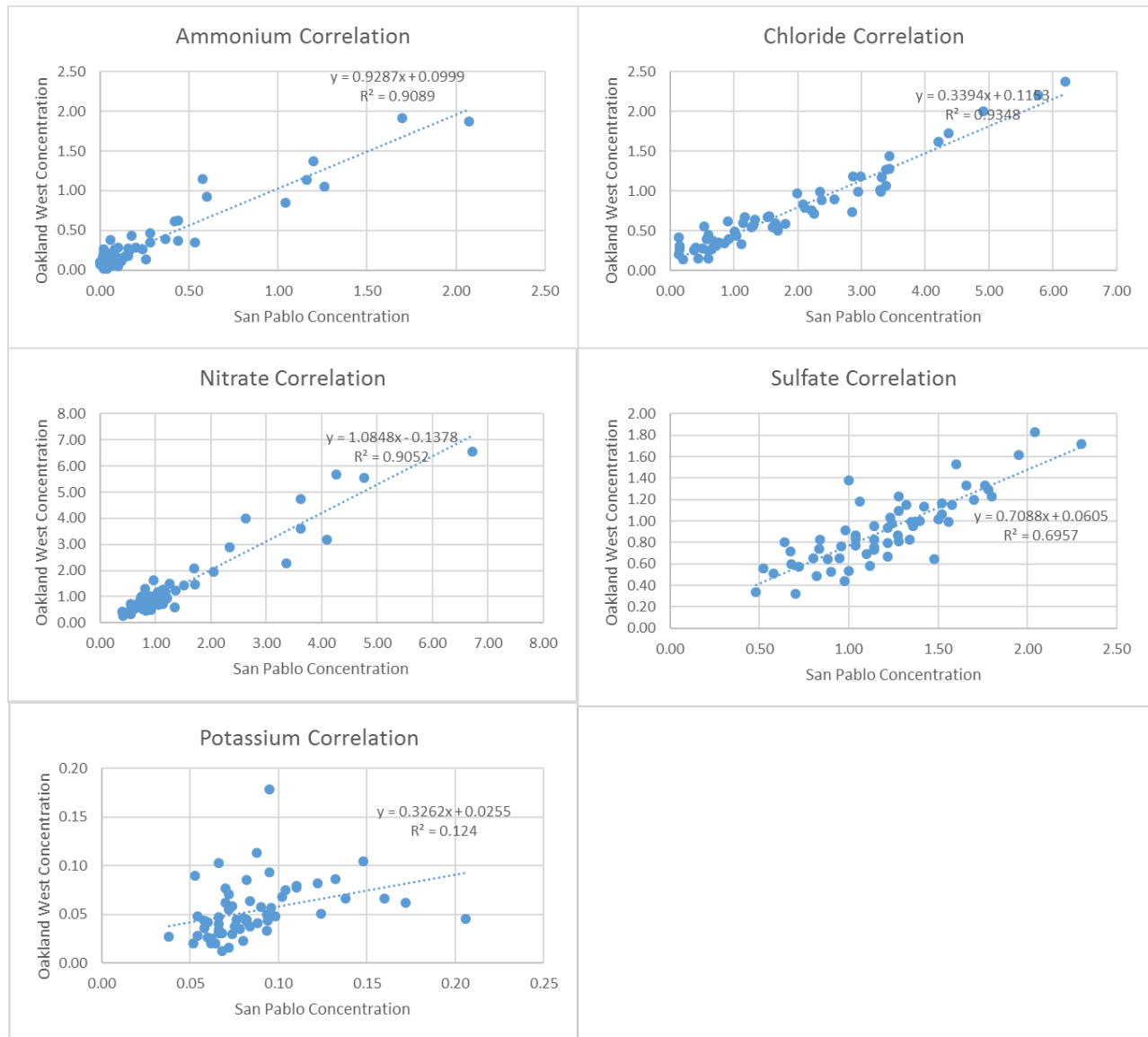
For the first pair of sites, San Pablo and Oakland West were chosen. San Pablo is a  $PM_{10}$  speciation air monitoring site, whereas Oakland West is a  $PM_{2.5}$  speciation air monitoring site. The correlation coefficient for Oakland West and San Pablo BAMs  $PM_{2.5}$  concentrations was 0.60. While not the best correlation coefficient, it still shows a good correlation between both sites and will serve as an acceptable comparison for the San Pablo  $PM_{10}$  speciation data. Figure 20 shows the time series graphs for the five ions of interest: ammonium, chloride, sulfate, nitrate and potassium. The graphs in Figure 20 shows that the ions trend well together.



**Figure 20.** Comparison graphs of ions for San Pablo and Oakland West.

In Figure 21, the correlation graphs for the five ions are shown. Apart from potassium, the other four ions are well correlated, with correlation coefficients ranging from 0.70 to 0.93. Potassium has a correlation coefficient of 0.12, showing that the potassium concentrations between the two sites are not well correlated. This could be because they are not at the same site, or that potassium varies more between size cuts of particulates.



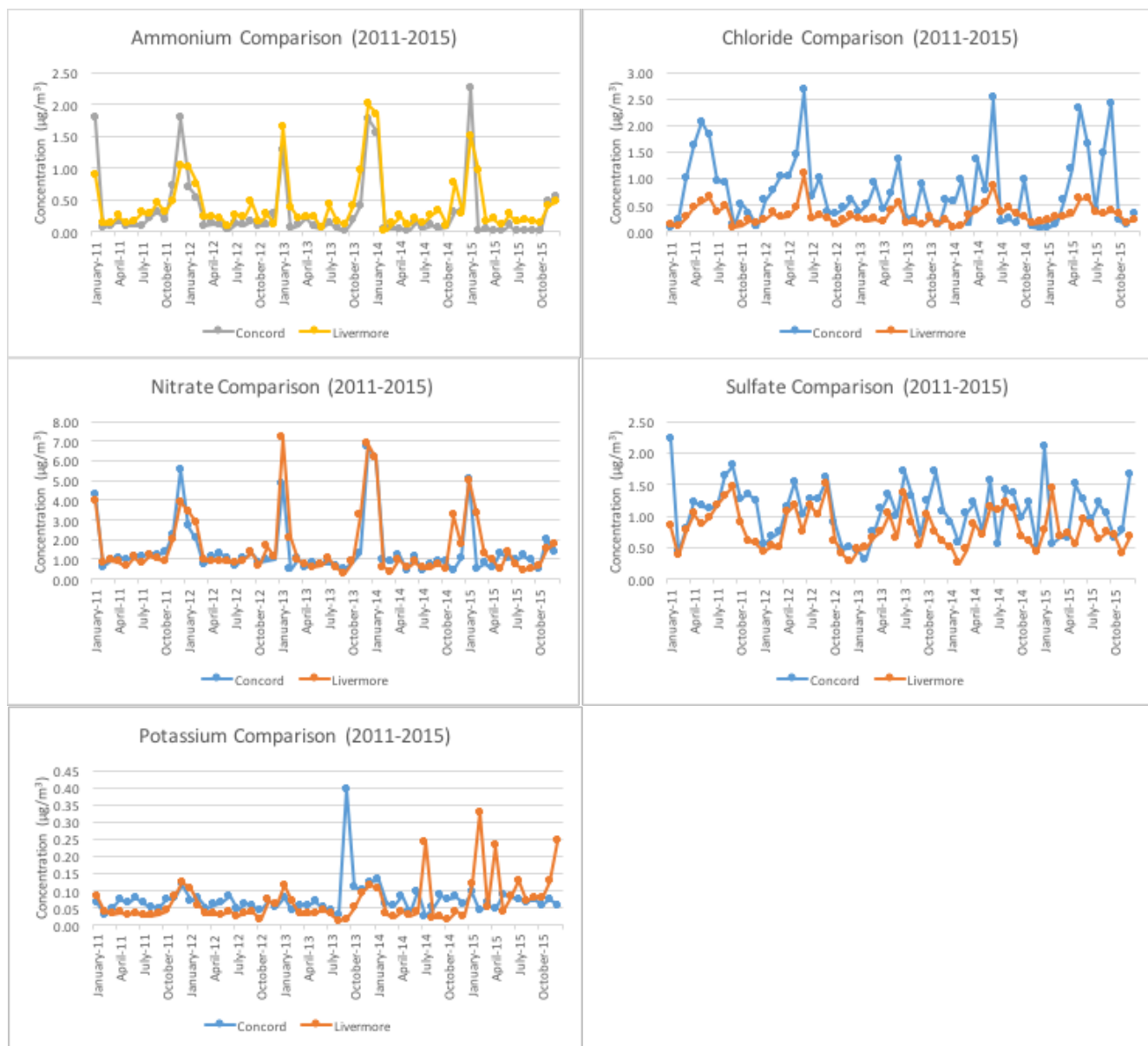


**Figure 21.** Correlation graphs for ions for San Pablo and Oakland West.

In both Figure 20 and Figure 21, the data indicates that four of the five ions are not only well correlated, but the ions are found primarily in the  $PM_{2.5}$  range of particulate matter, and not the  $PM_{10}$  range. Ammonium, chloride, and nitrate have strong correlation coefficients. Additionally, ammonium and nitrate have slopes in the correlation graphs of nearly one, indicating that the results are nearly identical. These two factors strongly indicate that these three ions are found in  $PM_{2.5}$  in the San Francisco Bay Area. Sulfate also has a good correlation coefficient, indicating that sulfate primarily is found in the  $PM_{2.5}$  range of particulates. Potassium is the only ion that does not appear to be strongly correlated. The potassium results could indicate that potassium is primarily found in the coarse range of particulates,  $PM_{10-2.5}$ , or that the

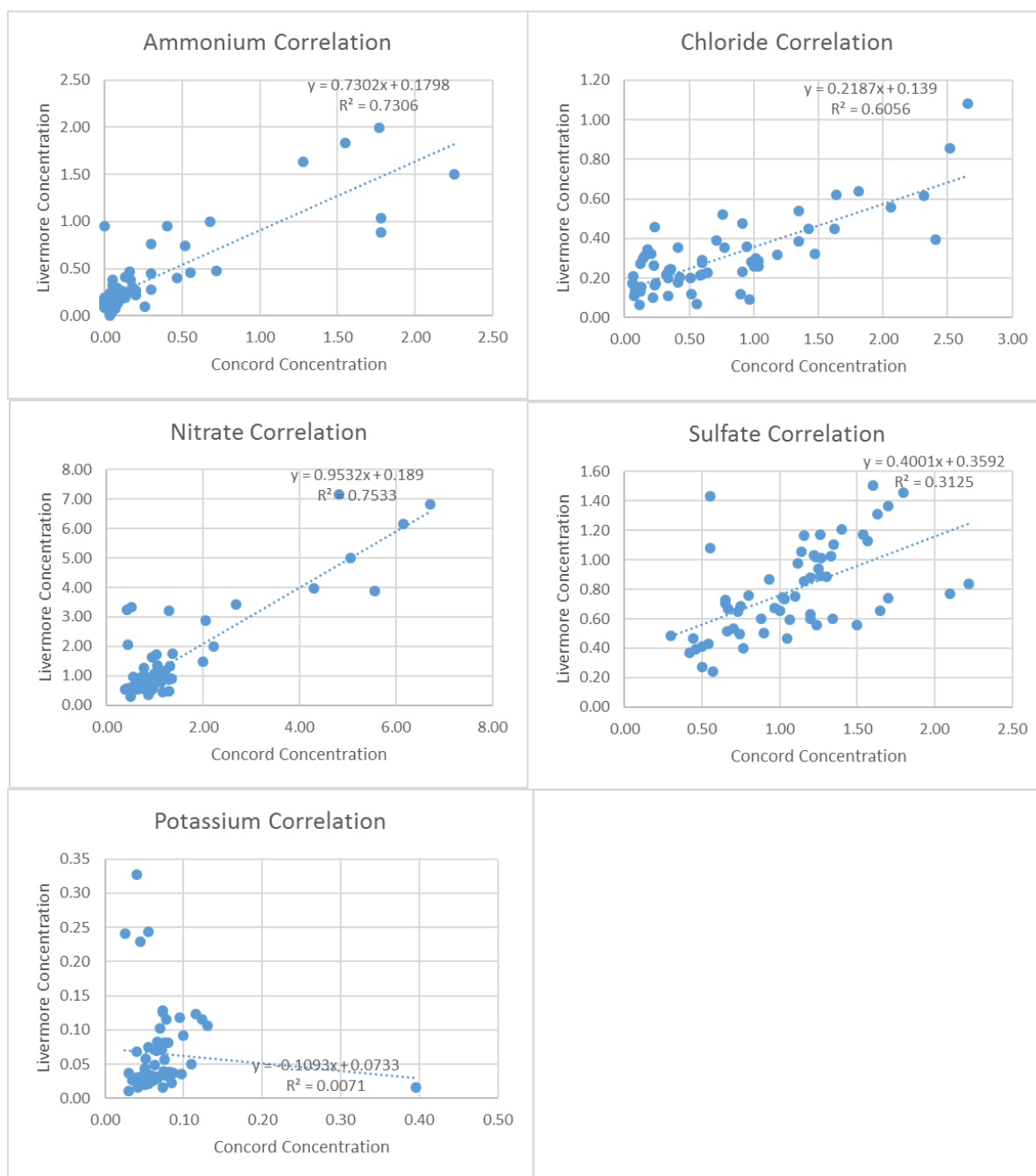
concentrations are low enough that any minor deviation would skew the data to indicate that the two are not correlated.

For the second pair of sites, Concord and Livermore were chosen. These two sites had a correlation coefficient of 0.77 for their BAMs PM<sub>2.5</sub> concentrations, which indicated a good correlation between the two sites. Concord has a PM<sub>10</sub> chemical speciation monitor, and Livermore has a PM<sub>2.5</sub> chemical speciation monitor. The times series graphs in Figure 22 show the trends of all five ions from 2011 through 2015.



**Figure 22.** Comparison graphs of ions for Concord and Livermore.

For all five ions, the concentrations trend well. Both ammonium and nitrate have almost the same concentrations for the entire five-year period. These results indicate that the ammonium and nitrate ions likely are components of  $PM_{2.5}$ , and not the coarse particulates,  $PM_{10-2.5}$ . The correlation graphs in Figure 23 shows that, except for potassium and sulfate, there is good correlation for the other three ions with correlation coefficients ranging from 0.61 to 0.75. These correlation coefficients indicate that it is possible that both  $PM_{10}$  and  $PM_{2.5}$  ion speciation may not be needed. In addition, for potassium and sulfate, it appears there are a handful of data points that could be viewed as outliers and the correlation coefficients would be much higher. Potassium concentrations are low, so any small difference can skew the correlation coefficient data.



**Figure 23.** Correlation graphs for ions for Concord and Livermore.

The data from Figure 22 and Figure 23 have some indication that the ions analyzed primarily reside in the fine particulates diameter size range. As previously mentioned, the correlation coefficient is good for the ammonium, chloride and nitrate, which is consistent with the analysis of Oakland West and San Pablo. Additionally, for potassium, the  $PM_{2.5}$  concentrations at Livermore were higher than the  $PM_{10}$  concentrations at Concord. If these two monitors were at the same site, the results would indicate that there was possibly an error in

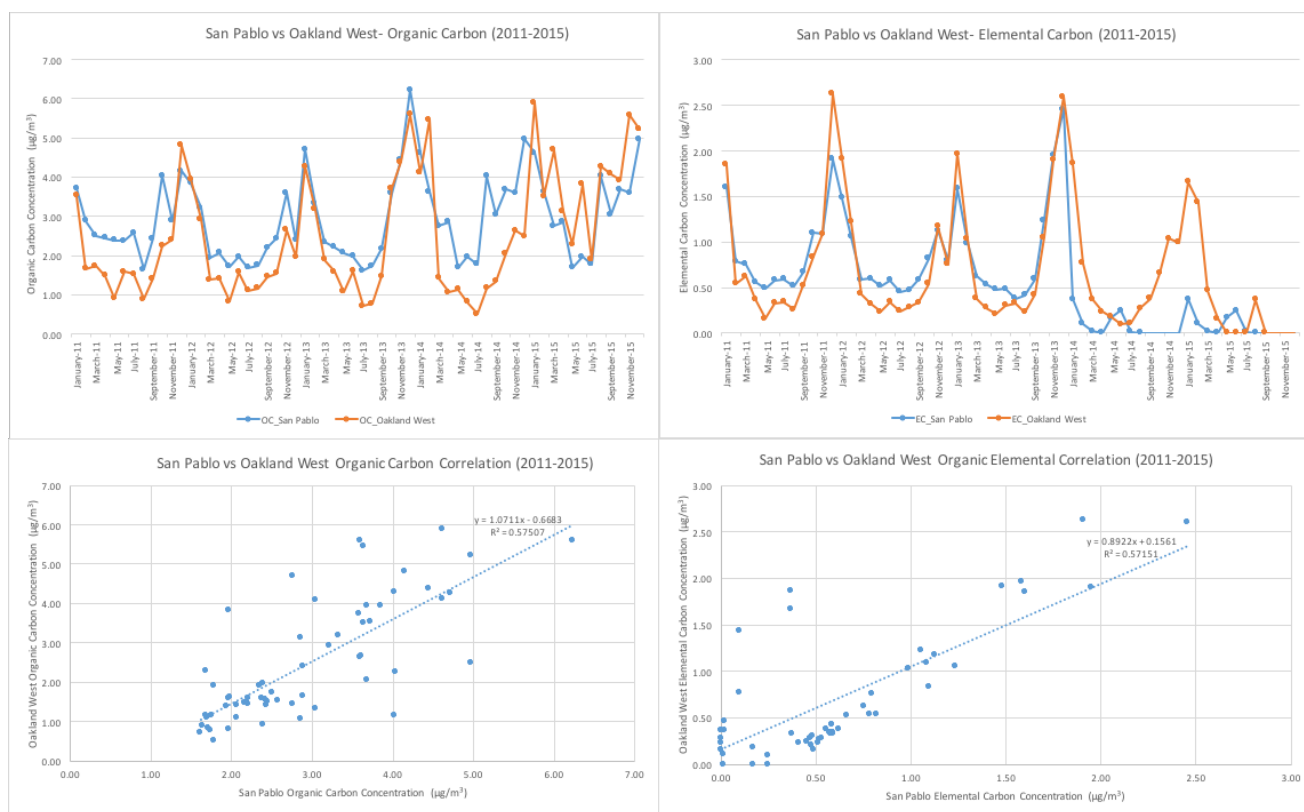
sampling, however because they are at different sites, the discrepancy could be due to different locations. It is possible that if the  $PM_{10}$  and  $PM_{2.5}$  speciation filters were at the same site the numbers might be more similar. The concentrations for ammonium and nitrate were nearly the same for the five-year period, indicating that ammonium and nitrate are primarily found in the  $PM_{2.5}$  range of particulates, and not in the  $PM_{10-2.5}$  size range. While the correlation coefficient is low for sulfate for the comparison of Livermore and Concord, the concentrations of sulfate are close to overlapping for the two sites for much of the five-year period studied in this paper.

The data from these two ionic speciation studies could indicate that chemically speciating both  $PM_{10}$  and  $PM_{2.5}$  for ionic compounds is redundant. While the potassium coefficient was not ideal for either site comparison, the potassium concentrations were low for both sets of sites, and thus any abnormally high concentration of potassium or any small discrepancy would skew the correlation data. For future studies, it would be useful to check the data for outliers to see if eliminating outliers would help with correlations. Additionally, it would be useful to be able to compare speciation components at the same site, rather than having to choose a nearby site that could have slight variations in data. The data indicates that ammonium, nitrate, and sulfate likely derive primary from  $PM_{2.5}$ , which agrees with some of the literature discussed in this paper. Chloride and potassium have shown to be more associated with the coarse particulates, than the fine particulates, but both chloride and potassium are both still found across the wide range of particulate matter diameter size. Ammonium, sulfate, and nitrate are primarily the result of combustion and secondary formations (gas to solid phase change) that are significant contributors to  $PM_{2.5}$ . Ammonium nitrate and ammonium sulfate are the secondary products that form. In contrast, chloride and potassium have some mechanical sources such as dust re-suspension, and soil and sea salt sources, that are primary contributors to  $PM_{10-2.5}$ . There are also sources of chloride and potassium for  $PM_{2.5}$ , which includes wood burning and combustion, like ammonium, nitrate, and sulfate. The ammonium and nitrate fluctuations during the winter season is likely due to an increase in wood and biomass burning that often occurs during the winter time due to the use of fireplaces and other wood-burning sources of heat, which agrees with literature discusses in this paper. Vehicle emissions contribute to ammonium, nitrate, and sulfate, and the contribution can be seen with the levels are seen throughout the year outside of the winter season. During the winter season, vehicle emissions do contribute to these ion concentrations, however vehicles are not the only source of these emissions. Both vehicle emissions and wood

burning contribute to these ions during the winter time, and meteorological factors such as inversion layers and wind speed and direction contribute to the particulates remaining in the atmosphere longer than during the rest of the year. Wood smoke contribution will vary by site, but vehicle emissions contribute to these ion emissions more consistently and widely.

### 5.3.3. CARBON COMPOSITION—ORGANIC AND ELEMENTAL (BLACK) CARBON

The same site pairings that were used for evaluating ion content, were used to evaluate carbon content. The carbon content will indicate how much vehicles and combustion are the cause of particulate matter. The first pair of sites to be compared are San Pablo and Oakland West. San Pablo is a PM<sub>10</sub> speciation site and Oakland West is a PM<sub>2.5</sub> speciation site. Figure 24 shows both the time series graphs for organic and elemental carbon comparing San Pablo and Oakland West and the correlation graphs for both organic and elemental carbon for San Pablo and Oakland West. The time series graphs show winter season fluctuations that are likely due to wood burning and weather patterns that would contribute to organic and elemental carbon residing in the atmosphere longer than during the other seasons. The organic and elemental carbon have similar concentrations throughout the five-year study period. There are some variations in elemental carbon concentrations starting in the second half of 2014.

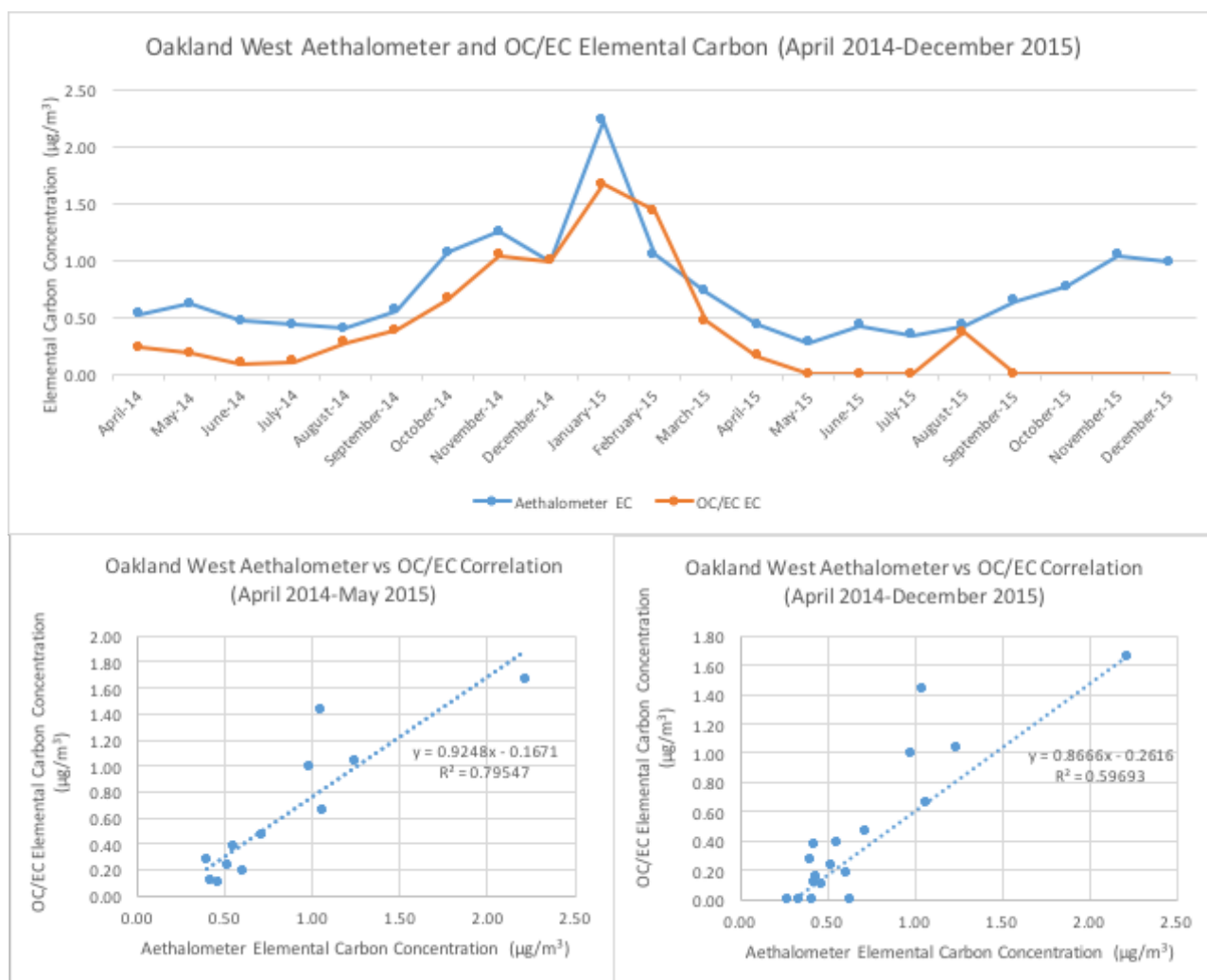


**Figure 24.** Time series and correlation graphs for organic and elemental carbon the comparison of San Pablo (PM<sub>10</sub>) and Oakland West (PM<sub>2.5</sub>).

The correlation graphs for both organic carbon and elemental carbon both showed a decent correlation, in fact both correlation coefficients were about 0.57. One issue to note is that in late 2014 when the laboratory switched to a new OC/EC, the elemental carbon data decreased in concentration to zero for most months. This could indicate that either the new instrument is less sensitive, meaning the instrument cannot measure accurately at low concentrations, or the new OC/EC calculated elemental carbon differently than the previous OC/EC. It is interesting to note that during the winter seasons there are elevated levels of organic and elemental carbon, which is consistent with possible sources of particulates in the winter time, such as wood and biomass burning. The results show that most of the organic and elemental carbon primarily appears in the PM<sub>2.5</sub> range because the PM<sub>10</sub> and PM<sub>2.5</sub> numbers are nearly the same in most instances. These results are consistent with the literature reviewed in this paper that showed organic and elemental carbon primarily fall in the fine particulate matter range, and not the coarse particulate matter range.

In addition to looking at data comparing PM<sub>10</sub> and PM<sub>2.5</sub> speciation data from the OC/EC, Oakland West also had an aethalometer that can be used to compare to the OC/EC to

decide if an aethalometer is a viable option for measuring elemental carbon continuously. Figure 25 shows the time series graph from April 2014 through the end of December 2015 of when data overlapped for the OC/EC and aethalometer at Oakland West.



**Figure 25.** Comparison of OC/EC and aethalometer for PM<sub>2.5</sub> elemental carbon at Oakland West.

The correlation graphs were separated into two different time frames: April 2014-May 2015 and April 2014-December 2015. This was done because May 2015 was when the Air District Laboratory switched to a new OC/EC. It was interesting to compare the correlation data from the old instrument and the correlation for the full 21 months of data. The correlation between the aethalometer and the OC/EC is better when looking at the correlation graph that uses just the old instrument data. When looking at the correlation data between the aethalometer and the entire study period that includes both new and old OC/EC, shows a worse correlation coefficient. These results could indicate that there is a sensitivity issue or calculation issue with

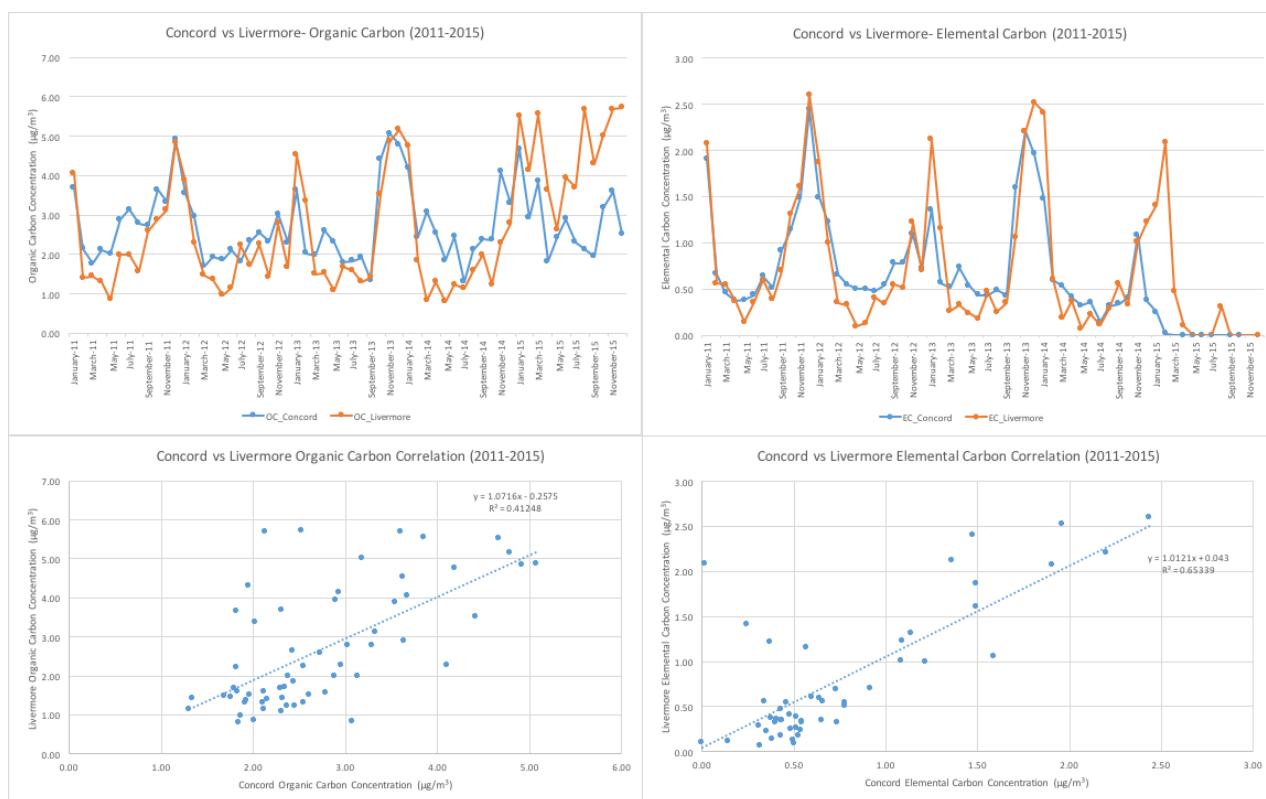


the newer instrument. The t-test results for the comparison of the PM<sub>2.5</sub> OC/EC results and the PM<sub>2.5</sub> aethalometer results in Table 7 indicate that there is no statistical difference. At 1% significance level, the t-test indicates that the two datasets are statistically the same, with the p-value being greater than 1%.

**Table 7.** T-test results for comparison of OC/EC to aethalometer at Oakland West from April 2014-December 2015.

	<i>Variable 1</i>	<i>Variable 2</i>
Mean	0.74	0.38
Variance	0.20	0.25
Observations	21	21
Hypothesized Mean Difference	0	
df	39	
t Stat	2.49	
P(T<=t) one-tail	0.01	
t Critical one-tail	1.68	
P(T<=t) two-tail	0.02	
t Critical two-tail	2.02	

In the next pairing, Concord and Livermore organic and elemental carbon were compared. Concord is a PM<sub>10</sub> chemical speciation site, and Livermore is a PM<sub>2.5</sub> chemical speciation site. In Figure 26, the organic carbon and elemental carbon time series and correlation graphs for Concord versus Livermore were plotted. The time series graphs show the trends for organic and elemental carbon from 2011 through the end of 2015. There are time periods where the organic and elemental carbon concentrations are almost the same for both sites, primarily during the winter months, which are likely due to wood burning and weather patterns that would contribute to organic and elemental carbon having a longer lifespan in the atmosphere than during the other seasons. The organic and elemental carbon have similar concentrations throughout the five-year study period. There are larger variations in elemental carbon concentrations starting in the second half of 2015, possibly due to a laboratory instrumentation change. The correlation graphs are shown in Figure 26. The correlation coefficient is low for the organic carbon datasets, and good for the elemental carbon datasets. However, the slope for both organic and elemental carbon in the correlation graphs are close to one, which would indicate that the two datasets produced the same results. This would contradict the correlation coefficient for organic carbon.



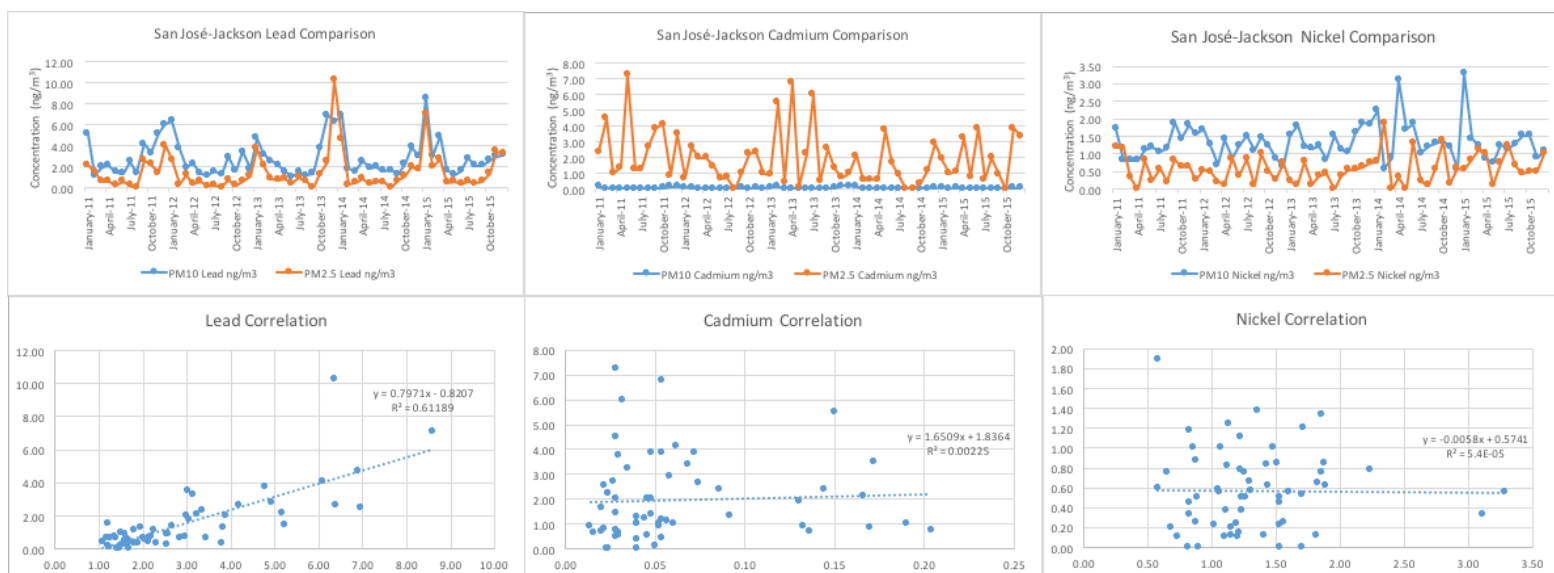
**Figure 26.** Time series and correlation graphs for organic and elemental carbon the comparison of Concord (PM<sub>10</sub>) and Livermore (PM<sub>2.5</sub>).

The carbon content data indicates that there are some similarities between PM<sub>10</sub> and PM<sub>2.5</sub> organic and elemental carbon content. The results indicated that at both sites the concentrations of organic and elemental carbon were close for most of the five-year study period. The seasonal fluctuations are likely due to an increase in wood burning, likely for heating purposes, and meteorological factors that contribute to vehicle emissions from remaining stagnant in the atmosphere. This data indicates that PM<sub>10</sub> elemental carbon and PM<sub>2.5</sub> elemental carbon do not both need to be monitored, but organic carbon might need to be monitored for both PM<sub>10</sub> and PM<sub>2.5</sub> because of the variability. However, literature has shown that organic and elemental carbon are primarily found in PM<sub>2.5</sub>, and not in the coarse range, PM<sub>10-2.5</sub>. It is possible that the discrepancy in this analysis is due to the different site locations of the PM<sub>10</sub> and PM<sub>2.5</sub> chemical speciation monitors. PM<sub>2.5</sub> monitoring of elemental carbon can be performed at more sites with the use of an aethalometer. The data from Oakland West indicated that the results from the OC/EC and aethalometer analysis of elemental carbon data were statistically similar and can be used as a comparable method of monitoring for elemental carbon, specifically in areas of concern where wood smoke and vehicle emissions are major contributors to elevated levels of

particulate matter. The literature studied in this paper indicate that a contributor to elemental carbon are vehicle emissions. The baseline level of elemental carbon that occurs throughout the year outside of the winter season is likely due to emissions from vehicles.

#### 5.3.4. METALS COMPOSITION

The last component of chemical speciation for PM<sub>10</sub> and PM<sub>2.5</sub> is metals composition at San José- Jackson. San José-Jackson has both a PM<sub>10</sub> and PM<sub>2.5</sub> chemical speciation monitor that collects speciation data, where the only overlap is metals. While there is the ability to analyze for more than 36 metals for both PM<sub>10</sub> and PM<sub>2.5</sub>, only three metals could be analyzed because of the availability of data. The three metals include lead, cadmium, and nickel. PM<sub>10</sub> metals were analyzed using an ICP-MS, whereas PM<sub>2.5</sub> metals were analyzed using an XRF. The data in Figure 27 shows that there is a stronger correlation with lead in PM<sub>10</sub> and PM<sub>2.5</sub> than with cadmium and nickel. The time series graphs in Figure 27 indicates that there is little to no cadmium found in the PM<sub>10</sub> filters, whereas a significantly higher concentration of cadmium was found in PM<sub>2.5</sub>.



**Figure 27.** Comparison and correlation graphs for lead, cadmium and nickel for PM<sub>10</sub> and PM<sub>2.5</sub> at San José-Jackson.

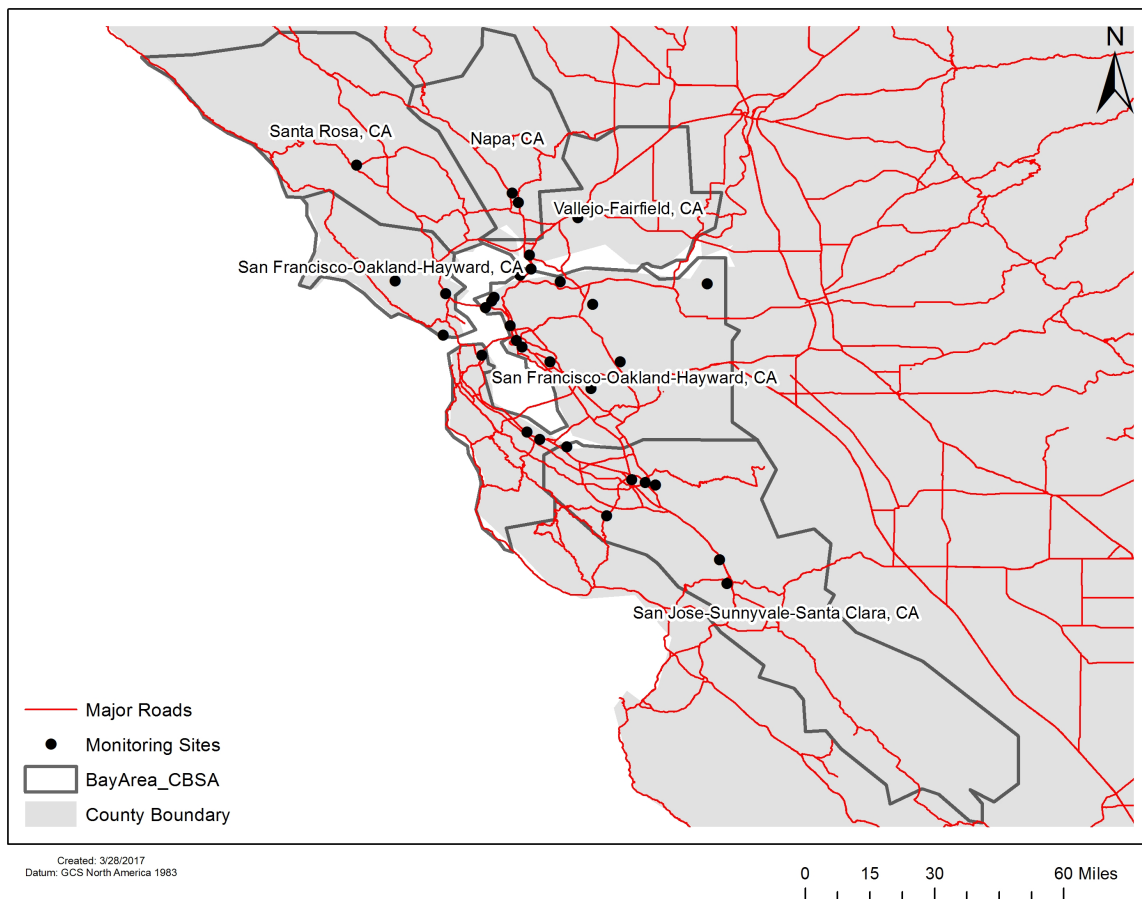
One possible reason for the significant different between the PM<sub>10</sub> and PM<sub>2.5</sub> cadmium concentrations could be due to the method of analysis. It should be expected that at least similar concentrations would be found for the metals, as PM<sub>2.5</sub> is a component of PM<sub>10</sub>, especially considering these samples were taken from the same site, unlike the previous analyses for ions and carbon content. However, this is not the case for this analysis. ICP-MS can be a more

sensitive method for analysis that XRF, meaning that it can measure more accurately at lower concentrations. For both cadmium and nickel, there is no correlation between  $PM_{10}$  and  $PM_{2.5}$ . These results indicated strongly that cadmium is primarily found in the fine particulates, whereas nickel varies a bit more, but is consistently higher in the  $PM_{10}$  dataset. The lead concentrations vary. In some instances, the lead concentrations are similar for both  $PM_{10}$  and  $PM_{2.5}$ . In a few instances, the  $PM_{2.5}$  lead concentrations were higher than the  $PM_{10}$  lead concentrations, which is a discrepancy in the data that can possibly attributed for the different laboratory instrumentation used to analyze the filters. The strong correlation coefficient between the  $PM_{10}$  and  $PM_{2.5}$  lead concentrations at San José- Jackson could indicate similar sources of emissions. These results are consistent with the literature. Metals are primarily found in the coarse particulates size cut range, as they are not usually the result of secondary reactions. Metals are the results of mechanical processes that infrequently result in the formation of fine particulates. Metals are found in the re-suspension of roadway dust, roadway degradation, soil, and tire and break wear.

#### 5.4. SOURCES OF PARTICULATE MATTER IN SAN FRANCISCO BAY AREA

The results from the Air District did provide some insight on sources and contributors to particulate matter. Looking at all the time series graphs from the Air District results, it appears that  $PM_{2.5}$  and  $PM_{10-2.5}$  contribute equally to particulate matter pollution in the San Francisco Bay Area. However, many of the chemical components appear to be more derived from  $PM_{2.5}$  than  $PM_{10-2.5}$ . With the exception of potassium and chloride, the three other ions appear to be primarily components  $PM_{2.5}$ . However, potassium and chloride do still contribute to  $PM_{2.5}$ , just not as significantly as they do to  $PM_{10-2.5}$ . In addition, the organic and elemental carbon content does appear to be more prevalent in the  $PM_{2.5}$  size cut than  $PM_{10-2.5}$  size cut of particulate matter. Cadmium also appears primarily in the  $PM_{2.5}$  size cut ranges, rather than in the  $PM_{10-2.5}$  size cut range, whereas nickel and lead is more prevalent in the  $PM_{10-2.5}$  size cut range. These results are consistent with the literature. The primary sources appear to be vehicle-related emissions, with some seasonal wood smoke. The ions and carbon content results indicate that there is a significant amount of vehicle related combustion occurring near the studied sites. In Figure 28, a map of all the major roadways in the San Francisco Bay Area are shown in relation to the particulate matter monitoring sites. There are numerous major roadways in the San Francisco Bay Area that are contributing to the  $PM_{2.5}$ .

## San Francisco Bay Area Major Roadways



**Figure 28.** Map of particulate matter sites in the San Francisco Bay Area with nearby roadways.

The 2011 Emissions Inventory published in 2014 is the most recent available emissions inventory published by the Air District. The report discusses how fluctuations in  $PM_{10}$  and  $PM_{2.5}$  concentrations are primarily due to construction and wildfires because of abnormally dry years due to drought (Fanai et al., 2014). According to the 2011 Emissions Inventory,  $PM_{2.5}$  in the San Francisco Bay Area primarily is the result of petroleum refining, chemical manufacturing processes, agricultural processes, stationary source combustion, off-road mobile sources, vehicles that weigh more than 6000 pounds, and accidental fires and cigarette smoke (Fanai et al., 2014).  $PM_{10}$  in the San Francisco Bay Area is the result of waste management processes, construction and farming operations, and paved and unpaved road dust (Fanai et al., 2014). Passenger cars and other vehicles that are less than 6000 pounds contribute an equal amount to

PM<sub>10</sub> and PM<sub>2.5</sub> (Fanai et al., 2014). The results from the study are consistent with the 2011 Emissions Inventory.

## 6. NETWORK REDESIGN AND RECOMMENDATIONS

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### 6.1. CURRENT METHOD OF NETWORK EVALUATION

The Air District is required to perform a thorough network assessment every five years for all criteria pollutants being monitored by the Air District (Bay Area Air Quality Management District, 2015; U.S. EPA, 2017c). The purpose of the network assessment is to ensure that the Air District meets the monitoring objectives listed in 40 CFR Part 58, Appendix D (Bay Area Air Quality Management District, 2015). There are six specific criteria that the Air District uses in order to assess if more sites need to be added to the monitoring network (Bay Area Air Quality Management District, 2015). The first criteria is to assess if the Air District meets the required minimum monitoring sites in each CBSA (Bay Area Air Quality Management District, 2015). The second criteria is to evaluate if all criteria pollutants that are non-attainment are being monitored in each county in the San Francisco Bay Area (Bay Area Air Quality Management District, 2015). The third and fourth criteria are locating the monitors that are the expected maximum concentration site for each pollutant and to located the background or pollutant transport sites (Bay Area Air Quality Management District, 2015). The last two criteria are to evaluate if the Air District will operate fewer monitors for pollutants in attainment and if more monitors are needed for non-attainment pollutants (Bay Area Air Quality Management District, 2015). The purpose of the network assessments are to evaluate the effectiveness of all the monitors in the Air District's air monitoring network and ranks how important each site is (Bay Area Air Quality Management District, 2015).

In the Air District's most recent network assessment published in 2015, the Air District evaluated all six criteria pollutants. Based on population size of the CBSA's in the San Francisco Bay Area and not exceeding the 24-hour NAAQS since 1991 for PM<sub>10</sub>, the Air District is required to have at least two SLAMS Sites each in only two CBSA's: San Francisco-Oakland-Fremont and San José-Sunnyvale-Santa Clara (Bay Area Air Quality Management District, 2015). The other three CBSA's are not required to have any PM<sub>10</sub> monitoring stations (Bay Area Air Quality Management District, 2015). One of the goals for the South Coast Air Quality Management District (SCAQMD) is to switch away from most filter-based monitoring and to more continuous based monitors to help improve forecasting and public access to data (Bermudez et al., 2016).

The Air District is currently meeting the minimum monitoring requirements as set forth by the EPA. Any changes to the particulate matter air monitoring network would need to be approved by the EPA, such as closing a site. The Air District needs to request EPA's approval for closing a SLAMS monitor, but not a SPM. The Air District would need to meet certain criteria to demonstrate that closing the monitor would not compromise the Air District's ability to demonstrate NAAQS compliance. The Air District would also need to confer with CARB to make sure closing a monitoring does not compromise the Air District's ability to demonstrate CAAQS compliance.

## 6.2. AIR MONITORING NETWORK RECOMMENDATIONS

The results in this study indicate that there are some management recommendations that need to be made. For the San Francisco Bay Area, most of the speciation components are more present in  $PM_{2.5}$  than in the coarse particulates. The primary exception is with the metals analysis. The metals analysis indicated that the metals are components of coarse particulates. The mass concentration results indicate that the coarse and fine particulate matter concentration are similar through most of the San Francisco Bay Area, with winter season increases in  $PM_{2.5}$  concentrations due to sources of emissions and weather patterns. These results indicate that for mass concentration, both  $PM_{10}$  and  $PM_{2.5}$  mass concentrations should still be monitored, however  $PM_{2.5}$  should be the priority because of health-related risks associated with fine particulates. Additionally, based on the Oakland West and Oakland East comparisons, only one of the sites is necessary. In looking at the other monitors at these two sites, it would make more sense to close the Oakland East side than the Oakland West site.

The ion analysis results could indicate that both  $PM_{10}$  and  $PM_{2.5}$  filters will still need to be chemically speciated. However, three of the five ions (ammonium, sulfate, and nitrate) indicate strongly that these ions are components of  $PM_{2.5}$  and not  $PM_{10-2.5}$ . Additionally, chloride is likely component of sea salt, which contributes significantly more to  $PM_{10-2.5}$  and not  $PM_{2.5}$ . Sea salt is not a significant health concern. Potassium is at a low concentration for both  $PM_{10}$  and  $PM_{2.5}$ , which is not concerning. These factors make it so that it would make more sense to spend more time chemically speciating  $PM_{2.5}$ , instead of chemically speciating as much as the Air District currently does.



The organic and elemental carbon analysis results also indicate that the Air District should shift focus to chemically speciating  $PM_{2.5}$  more so than  $PM_{10}$ . In the San Francisco Bay Area, organic and elemental carbon are primarily components of  $PM_{2.5}$ , and not  $PM_{10-2.5}$ . There appears to be minimal  $PM_{10-2.5}$  organic or elemental carbon. The organic and elemental carbon results indicate that monitoring carbon content in both  $PM_{10}$  and  $PM_{2.5}$  filters is not an effective use of resources. It would make sense for the Air District to stop carbon speciation of  $PM_{10}$  filters. Additionally, aethalometers could be implemented at more sites across the San Francisco Bay Area as a replacement for eliminating  $PM_{10}$  filter-based speciation.

The metals analysis results are not in agreement of the rest of the chemical speciation data. Lead and nickel both appear primarily in coarse particulate matter size range, with some overlap of lead and nickel in  $PM_{2.5}$ . Cadmium however, appears to primarily be found in the fine particulate matter size range. These results indicate that metals analysis should continue for  $PM_{10}$  filters because of information can be determined from analyzing the metals analysis on  $PM_{10}$  filters that are not available when analyzing the  $PM_{2.5}$  filters. Currently the only site that performs metals analysis on  $PM_{10}$  filters is San José- Jackson, which is a NATTS and NCore site. These are both EPA programs that the Air District would need to get special permission to stop analyzing for metals, which is unlikely to happen. The other  $PM_{10}$  sites do not currently have metals analysis performed on the filters.

The results indicate that it would be more effective to switch  $PM_{10}$  filter-based monitors to BAMs. This analysis shows that there is no reason to get rid of any of the  $PM_{10}$  sites, just convert the current filter-based  $PM_{10}$  monitors, except for the  $PM_{10}$  monitor in San José-Jackson, to BAMs monitors. South Coast Air Quality Management District, which is a similarly sized air district in California, currently uses BAMs to monitor for  $PM_{10}$  mass concentration, therefore it is reasonable to suggest the switch to BAMs. Additionally, replacing  $PM_{10}$  filter-based monitors with BAMs would allow for the Air District to calculate  $PM_{10-2.5}$  more reliably at more sites. Calculating  $PM_{10-2.5}$  using a  $PM_{10}$  filter and  $PM_{2.5}$  BAM data is not an accurate method of calculating coarse particulates.

Using BAMs to monitor for particulates allows for agencies to have a more thorough understanding of how particulate matter concentration varies throughout the day (Tao & Harley, 2014). In addition to having a more thorough understanding of how particulate matter concentration varies daily, monthly, quarterly, and even yearly. BAMs allows for more data to be

collected since the continuous monitors can sample down to the minute, whereas filter based samplers can only provide a small number of sampling days in comparison and does not have the ability to measure and show the concentration variations of particulate matter throughout the day. Additionally, having real-time data will potentially allow for better meteorological forecasting and better understanding of health effects (Tao & Harley, 2014). With minute and hourly data, it is possible to have a better understanding of how particulates are impacting people that work or live in specific areas near sources of particulates because looking at a 24-hour average does not necessarily apply well to epidemiological and toxicological studies. Data would be made available to the public quicker as well. For sites where chemical speciation for ions might be unnecessary, but elemental carbon analysis would be useful, aethalometers have shown to be a comparable method of monitoring continuously for elemental carbon in place of filters and laboratory analysis. The sampler head can also be switched to the desired size cut ( $PM_{10}$  or  $PM_{2.5}$ ) to analyze for elemental carbon.

In addition to removing  $PM_{10}$  filters, it would be interesting to add a  $PM_{2.5}$  speciation site in the northern region of the Air District, at a site like Napa, as there is currently no  $PM_{2.5}$  speciation site in the North Bay. Adding a  $PM_{2.5}$  speciation site at a site in the North Bay like Napa or San Rafael would allow for the chemical speciation of an area that tends to have higher wood smoke impacts, but is not in a valley that traps the wood smoke.

It would be prudent to evaluate the particulate matter air monitoring network on a regular basis. A system should be set up that would allow for better data analysis. Speciation is not readily available to compare as easily as mass concentration data. It would be helpful for agencies to set up a database, system and/or protocol that would allow for data to be uploaded to a centralized system and numbers could be compared between  $PM_{10}$  and  $PM_{2.5}$  much more readily.

There are limitations to the Air District implementing these recommendations. Adding a new monitoring site would take more time and resources than adding another monitor to an existing station, which is why the recommendation was made to add a  $PM_{2.5}$  speciation site to either Napa or San Rafael because those are already existing sites. Additionally, for any site close, the EPA would need to approve of the closure and the Air District would need to provide evidence that the site closures do not impact the Air District's ability to meet the NAAQS requirements. This study also did not factor in meteorological data from the San Francisco Bay

Area, which would give a more complete understanding of the sources of the pollutants. The last limitation is that the data was not normalized using the mass concentration. The next step of this analysis would have been to normalize the data and factor in the meteorological impacts. These factors would provide for a complete understanding of pollutant sources.

The next steps of this analysis aside from the previously mentioned normalization of data and factoring in meteorological data, would be to compare particulate matter concentration for both mass and chemical speciation components, across multiple sites in the San Francisco Bay Area. This analysis will allow for understanding on how pollutants are transported across the San Francisco Bay Area, and can provide a better understanding of where particulate matter is coming from. For example, it would be useful to compare metals or ions concentrations at all four PM<sub>2.5</sub> speciation sites to analyze whether there are spatial variations in the data that could give some insight into what the sources of particulates are in the San Francisco Bay Area.

## 7. CONCLUSION

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While this study has provided insight into the San Francisco Bay Area particulate matter air monitoring network, there are still areas where the data analysis could be improved. The main improvement could be in the availability of data to properly compare  $PM_{10}$  and  $PM_{2.5}$ , meaning having one site that has a complete chemical speciation set for both  $PM_{10}$  and  $PM_{2.5}$ , and to analyze both  $PM_{10}$  and  $PM_{2.5}$  using the same analytical technique, both laboratory and field instruments. By improving in these two areas, the evaluation of sources of  $PM_{10-2.5}$  and  $PM_{2.5}$  in the San Francisco Bay Area could be more accurate. The health impacts of the fine particulates outweigh the minor variations in the chemical speciation data, and it is important to chemically speciate  $PM_{2.5}$  in more areas to fully understand exposure and sources of  $PM_{2.5}$ . With the management recommendations, the San Francisco Bay Area would have a more complete understanding of sources of coarse and fine particulates.

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